

DEVELOPMENT OF HIGH TEMPERATURE THERMAL INSULATIONS USING TWO WASTE MATERIALS : THERMIT SLAG AND RICE HUSK ASH

A Thesis Submitted
in Partial fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

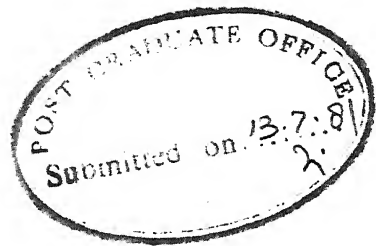
By
V. VIJAYA BHASKAR

to the
DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JULY, 1981

I.I.T. KANPUR
CENTRAL LIBRARY

Acc. No. **A 66859**

SEP 1981



ii

CERTIFICATE

This is to certify that this work entitled
"DEVELOPMENT OF HIGH TEMPERATURE THERMAL INSULATIONS USING
TWO WASTE MATERIALS : THERMIT SLAG AND RICE HUSK ASH" by
V. Vijaya Bhaskar has been carried out under my supervision
and has not been submitted elsewhere for a degree.

A handwritten signature in dark ink, appearing to read "P. C. Kapur".

Dr. P. C. Kapur
Professor

Department of Metallurgical Engineering
Indian Institute of Technology
Kanpur.

Kanpur
July 1981.

POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
Master of Technology (M. Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur
Dated.

ACKNOWLEDGEMENTS

I take the opportunity to express my deep sense of gratitude and profound regards to Dr. P.C. Kapur for his invaluable guidance and constant encouragement which were vital to the success of this work.

I am very thankful to Messrs R.K. Prasad, O.P. Malviya and B. Sharma, for their assistance throughout the experimental work. My sincere thanks are also due to Messrs M.V. Subhash Bose, K. Ramesh Chowdary and V. Satish, for their help in the completion of this work.

I am thankful to Mr. R.N. Srivastava for his efficient typing of this thesis and Mr. V.P. Gupta for his efficient tracing of the graphs.

Lastly, I would like to thank all my friends who made my stay at I.I.T. Kanpur a pleasant one.

- Vijaya Bhaskar

CONTENTS

<u>CHAPTER</u>	<u>Page</u>
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	.
1. INTRODUCTION	2
2. LITERATURE SURVEY	3
2.1 Thermal Insulations	3
2.2 Rice Husk Ash	5
2.2.1 Mullite	9
2.2.2 Thermit Slag	12
2.3 Bonds	13
2.3.1 Phosphate Bonding	13
2.3.1.1 Phosphoric Acid	14
2.3.2 Sodium Silicate	15
2.3.3 Ashment Cement	15
3. OBJECTIVES OF THE PRESENT WORK	19
4. MATERIALS AND METHODS	20
4.1 Materials	20
4.1.1 Rice Husk Ash	20
4.1.2 Thermit Slag	27
4.1.3 Alumina	29
4.1.4 Pop Corn	29
4.1.5 Chemical Bonds	29
4.2 Methods	30
4.2.1 Grinding	30
4.2.2 Disc and Cube Samples	30
4.2.3 Mixing Procedure	31
4.2.4 Hardening and Curing	32
4.3 Testing	32
4.3.1 Porosity	32
4.3.2 X-ray Diffraction	33
5. PRELIMINARY TRIALS	34
6. RESULTS AND DISCUSSION	37
6.1 Lightweight Thermal Insulation Materials from Thermit Slag	37

<u>CHAPTER</u>	<u>Page</u>
6.1.1 Sodium Silicate Bonded Thermal Insulations	37
6.1.2 Phosphoric Acid Bonded Thermal Insulations	37
6.1.2.1 The Effect of Temperature on Shrinkage (Linear and Volumetric), Bulk Density and Strength	39
6.2 Mullite Insulations	42
6.2.1 Effect of Soak Time at 1450°C on the Shrinkage, Porosity and Tensile Strength of Mullite Insulating Bricks	45
6.2.1.1 Shrinkage	45
6.2.1.2 Porosity	45
6.2.1.3 Tensile Strength	47
6.3 Ashment Bonded Rice Husk Ash Insulations	47
6.3.1 The Effect of Temperature and Amount of Bond on Shrinkage, Strength, Hydration and Bulk Density of Ashment Bonded Insulation Bricks	49
6.3.1.1 Shrinkage	49
6.3.1.2 Strength	50
6.3.1.3 Hydration	50
6.3.1.4 Bulk Density	53
6.3.2 Effect of Soak Time on the Shrinkage and Porosity of the Ashment Bonded Insulations Fired at 1200°C	55
6.3.2.1 Shrinkage	55
6.3.2.2 Porosity	55
7. CONCLUSIONS	57
REFERENCES	59
APPENDIX-1. Experimental Measurements	61

LIST OF TABLES

	Page
2.1 Chemical properties of rice husk and rice husk ash	5
2.2 Properties of mullite	11
2.3 Chemical analysis of the thermit slag	12
2.4 Compressive strength of 1:3 cement sand cubes	18
4.1 Colour of the heat treated rice husk ash	26
4.2 Experimental parameter for XRD-5	33
5.1 Setting time and relative strengths for ground thermit slag with different chemical bonds at room temperature	35
5.2 Relative strength of thermit slag with different chemical bonds, fired to different temperatures	36
6.1 Compositions of mullite mixtures	43

LIST OF FIGURES

		Page
2.1	Variation of the particle size (diameter) of the rice husk ash silica with temperature of thermal treatment	8
2.2	Differential scanning calorimetric analysis of the rice husk ash fired at 1200°C for 3 hours	8
2.3	The relative cold compressive strengths of portland cement after subjection to heat	17
4.1	Tube-in-basket furnace	21
4.2	Experimental set up for the constant temperature environment furnace for rice husk burning	21
4.3	Temperature variation in the husk bed at constant temperature environment, with time	23
4.4	Thermogravimetric analysis on rice husk ash fired at different temperatures	24
4.5	X-ray data on heat treated rice husk ash at different temperature	25
4.6	Variation in true density of rice husk ash with firing temperature	28
6.1.1	Variation of bulk density as a function of slag/pop corn ratio	38
6.1.2	Effect of firing temperature on shrinkage and bulk density of phosphate bonded lightweight insulation discs	40
6.1.3	Variation of compressive load with deformation for 40% phosphoric acid bonded thermit slag lightweight insulation discs fired to various temperature	41
6.2	X-ray data on mullite insulations fired at 1450°C with time	44
6.2.1	Variation of shrinkage and porosity as a function of soak time for mullite insulation discs	46

6.2.2	Variation of tensile strength as a function of soak time for mullite insulation discs	48
6.3.1	Variation of shrinkage and compressive strength as a function of temperature for hand moulded ashment bonded rice husk ash insulation cubes	51
6.3.2	Variation of shrinkage and tensile strength as a function of temperature for machine pressed ashment bonded rice husk ash insulation discs	52
6.3.3	Variation of bulk density and hydration as a function of firing temperature for ashment bonded rice husk ash insulation discs	54
6.3.4	Variation of porosity and shrinkage as a function of soak time for ashment bonded rice husk ash insulation discs fired at 1200°C	56

ABSTRACT

The thermit slag, which is a high alumina, high refractory waste material was effectively used to develop ultra-lightweight thermal insulations using 40% phosphoric acid bond and pop corn to induce the porosity in the brick. After prefiring at 800°C the bricks can be conveniently used upto 1100°C with good strength properties.

A cheap, abundant waste material rice husk ash was used for development of porous mullite insulations and ashment cement bonded bricks. The former has on average 60% porosity and quality to resist temperatures as high as 1600°C with an excellent dimensional stability. These mullite insulations can be used as hot face insulating material. The latter, i.e. ashment bonded bricks, can be used either in the form of blocks or as an insitu ramming mass. It was observed that with increase in ashment cement content in ash, there occurred an increase in strength, and shrinkage with increase in the temperature of firing. The variation in the porosity and shrinkage remained near constant when bricks fired at 1200°C for prolonged times.

CHAPTER - 1

INTRODUCTION

This thesis deals with the manufacture of high temperature refractory insulations in the form of bricks and hollow spheres (bubbles, which can be conveniently used as packing material for loose fill insulation) from two waste materials - thermit slag and rice husk ash. The thermit slag was ground and bonded with either sodium silicate or phosphoric acid and smeared (coated) around exfoliated pop corn which on firing gave insulating hollow spheres. Alternately, the coated pop corns were cast into the shape of a brick and fired, resulting in a light weight insulating brick.

Rice husk ash a highly porous material, was reacted with calcined alumina in stoichiometric proportions to form porous mullite. Alternately rice husk ash was bonded with hydraulic setting ashment cement which has a very low percentage of free lime in it.

At present, insulations tend to be expensive. There is a need to develop cheap insulations using simple technology which can be adopted widely. Therefore, the rationale behind this work is to (1) develop thermal insulation for conservation of energy, (2) use waste materials for this insulations which are cheap and (3) device manufacturing processes which are simple and relatively cheap.

CHAPTER - 2

LITERATURE SURVEY

The literature survey here is restricted to areas which are relevant to and impinge upon the present work, namely

- (1) Various kinds of thermal insulations available
- (2) Raw materials: Thermit slag and Rice husk ash
- (3) Chemical bonds: Sodium silicate, Phosphoric acid and Hydraulic setting cement, particularly ashment cement.

2.1. THERMAL INSULATIONS

There are two kinds of high temperature thermal insulation, hot face and cold face. Hot face insulations are those directly exposed to the interior of the furnace whereas cold face insulations are back up lining for the dense refractory. Thermal insulations lead to conservation of heat. In view of the limited resources of fossil fuels and increasing rate at which they are being consumed, insulations have become increasingly important in recent years.

Thermal insulations of the furnace help in reducing the heat loss through certain parts of the structure. The resultant saving in fuel frequently more than compensates for the extra materials' cost involved. A disadvantage is that insulations rarely add to the refractory life, and indeed may even reduce it.⁽¹⁾

Whether the use of insulation is justified or not depends on:

- (1) The anticipated fuel saving, which can be generally calculated and occasionally checked,
- (2) The increase/decrease in the output of the furnace,
- (3) The increase/decrease in the cost of refractories including insulation, and
- (4) The cost of alteration to the foundation or steel work necessary to permit insulation.

For the manufacture of thermal insulations one starts with two kinds of materials: (1) those which are inherently porous, hence can be converted into insulation brick directly by either bonding with some bond or by cutting into suitable bricks and shapes, if the material is available as chunks, and (2) those materials which are relatively dense and therefore porosity is imparted by external means. Examples of inherently porous materials are diatomites, asbestos, ⁽²⁾ exfoliated vermiculite etc. A particularly promising natural porous material is rice husk ash which has been exploited in this research work. In theory any dense refractory material can be converted into high temperature thermal insulation by imparting porosity to it. Examples are clay, silica, sillimanite, alumina etc. In the present work thermit slag has been used, which is a high aluminous, high refractory and a waste material.

2.2. RICE HUSK ASH

Rice husk ash, an agricultural waste material, is available in large quantities in the paddy growing countries at little or no cost. This ash is highly porous, mostly silica and possesses refractory and thermal insulation properties. Currently, the world-wide production of rice exceeds 370 million tonnes per annum. Nature has provided the rice grain with a tough, highly silicious woody outer coat, called rice husk or hull, for protection in the course of its maturity. Rice husk is 4 to 5 mm in length, 1 to 2 mm in width and about 0.5 mm thick. Its bulk density is very low, 95 to 150 kg/m³. Depending on the paddy strain, soil, climatic conditions and the agricultural practices employed the composition of rice husk varies as shown in Table 2.1.

TABLE 2.1. Chemical Properties of Rice Husk and Rice Husk Ash.⁴

Ultimate analysis of rice husk (wt %)		Chemical analysis of rice husk ash (wt %)	
Ash	: 16 - 25	SiO ₂	: 87 - 97
Carbon	: 38 - 42	K ₂ O	: 0.6 - 2.5
Hydrogen	: 4.5 - 5.5	Na ₂ O	: trace - 1.75
Nitrogen	: 0.3 - 2.0	CaO	: 0.2 - 1.5
Sulphur	: 0.07 - 0.12	MgO	: 0.1 - 1.95
Oxygen	: 30 - 32	Fe ₂ O ₃	: trace - 0.55
Moisture	: Rest	P ₂ O ₅	: 0.2 - 2.8

The fuel value of rice husk lies in the range of 3000 to 3600 K cal/kg, which is about one-half the calorific value of good quality coal. One ton of harvested paddy yields about 200 kg rice husk, which on complete combustion leaves behind roughly 40 kg of an inorganic residue, namely, rice husk ash, the composition of which is shown in Table 2.1. Depending on the time and temperature of combustion and the impurities present, the silica either remains in an amorphous phase or is transformed into its various polymorphic modifications - quartz, tridymite or cristobalite. These aspects are dealt in detail below. The refractoriness of rice husk ash depends primarily on its alkali oxide content. However, it is normally as high as 1600°C. Rice husk ash is a highly porous, light-weight and bulky material; the loose and tapped bulk densities are 210 to 300 kg/m³ and 280-400 kg/m³, respectively. Therefore it is ideally suited for thermal insulations.⁽³⁾

Hanafi et.al.⁽⁵⁾ have reported the phase changes in amorphous silica in rice husk ash. Silica samples were prepared by firing rice husk at various temperatures ranging from 500 to 1400°C at 100°C interval for 3 hours. The crystalline modifications in rice husk ash were detected by X-ray diffraction analysis. He reports that, no crystalline modifications were detected on heating rice husk upto 800-900°C; at 900°C, the nucleation process for the formation of the low-form of cristobalite phase was pronounced. As the temperature increased to 1000°C, a sharp increase in the

crystalline size of the silica grain was observed (Figure 2.1). The tridymite phase begins to crystallise on heating rice husk at 1200°C, whereas at 1300 and 1400°C the well ordered hexagonal form of tridymite makes its appearance besides the cristobalite phase. The beginning of crystallisation of tridymite is associated with minor decrease in the crystallite size of the silica grain produced at 1200°C. However, the ordered hexagonal form obtained at 1300 and 1400°C is accompanied by an increase in the crystallite size to a characteristic value.

Hanafi et.al.⁽⁵⁾ have also shown the Differential Scanning Calorimetric (DSC) thermogram for the ash sample fired at 1200°C for 3 hours (Figure 2.2). It demonstrates the existence of an exothermic peak at 135°C, which represents the transformation of the tridymite phase ($T_p - T_e$), and four endothermic peaks located at 190, 220, 235 and 250°C representing the transformation of the cristobalite phase ($C_a - C_p$). The three endotherms located at 190, 220 and 235 represent the transformation of the low form unordered cristobalite, whereas the endotherm located at 250°C represents the transformation of the well ordered crystalline form.

Latter Ibrahim et.al.⁽⁶⁾ have also supported the Hanafi's theory of crystallisation of rice husk ash by infrared spectroscopy. The ratio of the absorbancy bands corresponding to the Si-OH and Si-O groups occurring at 810 cm^{-1} gave the amount of Si-OH left undestroyed at each firing temperature. The OH group of rice husk ash was lost at about 700°C.

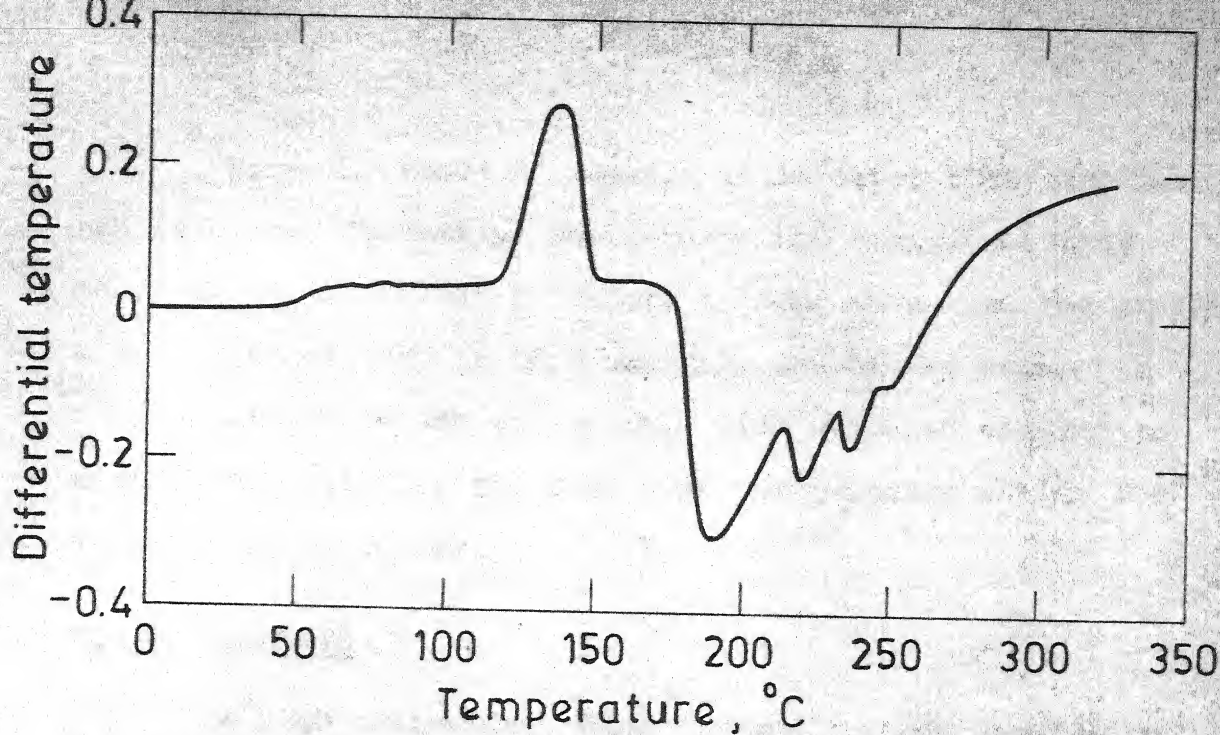


Fig. 2.2 - Differential scanning calorimetric analysis of the rice husk ash fired at 1200 °C for 3 hrs.

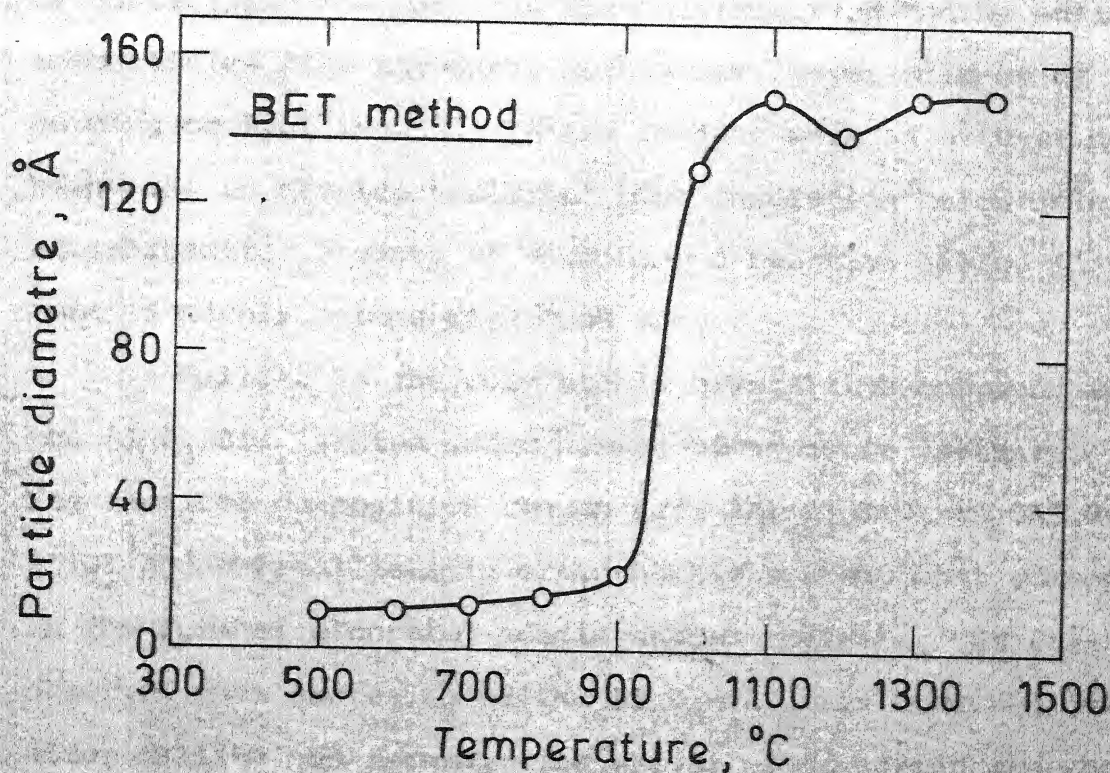


Fig. 2.1 - Variation of the particle size (diameter) of the rice husk ash silica with temperature of thermal treatment.

From the above discussion it is clear that rice husk ash is a very attractive and perhaps the best insulating material available and therefore a major thrust of the present work was to utilise it in a suitable insulating form.

Rice husk ash was reacted with calcined alumina to form porous mullite, the rice husk ash provides silica for reaction and porosity.

2.2.1. MULLITE

A high refractory, high alumina thermal insulation brick can be manufactured from kyanite or sillimanite type base materials. The porosity of the brick may be achieved by controlling the particle size distribution and by adding combustibles like saw dust, anthracite, paper pulp or by foaming or frothing.⁽¹⁾ In the present work an attempt has been made to develop "mullite" base insulation brick using stoichiometric amounts of alumina and reactive silica in the form of highly porous rice husk ash.

Mullite is the only stable crystalline compound in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system under normal atmospheric pressure. Its chemical composition ranges from $2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ to $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and crystallizes in orthorhombic system, most commonly in the form of elongated needle-shaped crystals. It was observed that sintering of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ mix occurred only after mullite has formed. The arrest of sintering was thought to be caused by expansion and formation of a mullite "framework".⁽⁷⁾ In $\text{Al}_2\text{O}_3\text{-SiO}_2$ pellets, the conversion of quartz to

cristobalite caused the silica to expand, thus exerting strong pressure and establishing good contact with neighbouring Al_2O_3 , and forming mullite by diffusion of Al_2O_3 into silica zone, a glass phase was formed surrounding cristobalite. However, mullite crystals were found to grow along the c-axis parallel to the direction of diffusion as a result of the movement of SiO_2 into Al_2O_3 .

Stately⁽⁸⁾ noted that rate and degree of formation of mullite in powder mixtures increased at about the same rate as corundum decreased, and thus inversely dependent on the instantaneous particle size of the alumina phase.

A good mullite brick should contain an average of 85% mullite. The glass content should not exceed 5%, and it should be highly silicious so that its viscosity is high. Usually some unreacted Al_2O_3 is also present.⁽⁹⁾ As one approaches the mullite composition 72% Al_2O_3 - 28% SiO_2 , the percentage of vitreous phase decreases and the properties of refractory material improves. Increase in Al_2O_3 content to about 75% results in (1) resistance to slag attack, (2) greater spalling resistance, and (3) general decrease of the iron oxide corrosion.⁽¹⁰⁾ The properties of mullite are shown in Table 2.2.

Kapur⁽³⁾ has also shown that it is possible to make very cheap thermal insulations of type hydraulic setting calcium silicate/silica. Rice husk ash is a pozzalana-par-excellence. When 65 to 75% ash is ground very finely with 25-35% dry hydrated lime, the resulting mixture is known as

TABLE 2.2. Properties of Mullite.⁽⁷⁾

Structural properties			Chemical properties	
Crystal structure	Orthorhombic		Chemical nature	Slightly acidic
Theoretical density (gm/cc)	3.16 - 3.22		Limit of usefulness (°C)	
			in air	1800
Melting point (°C)	1850		in vacuum	1500 - 1700
Hardness (mhos)	7.5		Stability	
Crystal habit	Acicular or prismatic		in reducing atmosphere	Fair
			in carbon	Fair
Positions and intensities of three strongest X-ray reflections	d	I/I ₀	in acid slag	Good
	3.42	10	in basic slag	Fair
	2.21	8	in metals	Fair
	1.53	8	in most acids	Insoluble

Ashmoh⁽¹¹⁾. (1) It is a hydraulic cement which sets by forming hydrated calcium silicates, including tobermorite type phase. (2) It binds unground rice husk ash quite well, when the latter is used as a light-weight aggregate. Ashmoh - rice husk ash concrete in 1:1, 1:2, 1:3 weight ratios was used in producing thermal insulations after curing for 28 days under water. Although somewhat low in strength, these are exceptionally cheap and simple to make concretes, in form of either monolithic constructions or blocks, could be useful for thermal insulation of driers, ovens, chimneys etc.

The problem with this form of insulations where Portland Cement or Ashmoh Cement is used, is the presence of

free Ca(OH)_2 which loses water around 550°C to form CaO . On cooling CaO forms Ca(OH)_2 causing 44% volume expansion which results in disruption of the structure. Clearly if a hydraulic setting bond can be used, which does not have free lime, this problem can be eliminated. In this present work such a bond, "ashment" cement has been used.

2.2.2. THERMIT SLAG

Thermit slag is produced in the manufacture of ferro-alloys by reduction of FeO mixed with chrome ore, manganese ore, tungsten ore etc., in the presence of CaO ; aluminium powder provides heat for the fusion process by reduction of oxide ores. The typical analysis of the slag is in Table 2.3.

TABLE 2.3. Chemical Analysis of the Thermit Slag (wt %).

SiO_2	2.10	CaO	6.0
FeO	0.16	MgO	0.9
Al_2O_3	80.30	MnO	10.1

It is seen that the slag is high in alumina, though its refractoriness could not be measured in our laboratory, it is easily in excess of 1650°C and therefore it is an attractive raw material for high temperature thermal insulation. This thermit slag is also a waste product.

In the present work, the bonding of ground thermit slag was tried out with sodium silicate and phosphoric acid.

2.3. BONDS

Chemical bonding in refractory industry is gaining importance day by day owing to their many advantages over the ceramic bond. In the present work on the development of thermal insulation materials, phosphate, sodium silicate and hydraulic setting cement bonds were tried. These are discussed below.

2.3.1. PHOSPHATE BONDING

According to Kingerey⁽¹⁴⁾ phosphate bonding can be accomplished by (1) using silicious materials with phosphoric acid, (2) using metal oxides with phosphoric acid and (3) by direct addition or formation of acid phosphate.

These methods are widely used in addition to ammonium phosphate, chromium-aluminum phosphate, alkali metaphosphate, magnesium acid phosphate, aluminum chloro phosphate hydrate acid, mixtures of aluminum phosphate and urea phosphate. Phosphoric acid and solutions of mono aluminum phosphate (MAP) are most frequently used bonds. The alkali phosphates are particularly useful in bonding basic aggregates (phosphoric acid and MAP solution react too fast). Use of chromium acid in conjunction with phosphoric acid significantly enhances the strength of a sample fired at 1300°C. Bond phase inversions, characteristic in aluminum phosphate systems were

significantly reduced due to formation of stable phases in aluminum-chromium phosphate bonded bodies.⁽¹⁵⁾ A strength enhancement of about 25% was observed by Roy et.al.⁽¹⁶⁾ over a wide range of high temperatures.

2.3.1.1. PHOSPHORIC ACID

Phosphoric acid reacts with metal oxides and hydroxides at 20°C to 200°C to form a hard solid. Although hardening system based on H_3PO_4 and TiO_2 , CaO , FeO , Fe_2O_3 , NiO , ZnO , ZnO_2 , MgO , Al_2O_3 and Cr_2O_3 were investigated, the system H_3PO_4 - Al_2O_3 has been studied most extensively. The phases formed when H_3PO_4 reacts with Al_2O_3 and $Al(OH)_3$ are similar. It is generally agreed that, in these reactions, acid phosphate of the type $Al(H_2PO_4)$ are formed initially, subsequent heating in the presence of excess Al_2O_3 produces a final bonding phase which is almost certainly $AlPO_4$.⁽¹⁷⁾

Direct calorimetric analysis (DCA) studies⁽¹⁵⁾ of the reactions of Al_2O_3 with H_3PO_4 show that bonding begins at approximately 127°C. Most of the reaction occurs over the range 127-427°C involving formation of aluminum phosphates and possible formation and melting of pyro phosphoric acid, at approximately 510°C. Between 732°C to 1327°C transformation and crystallization of aluminum phosphate bonding phases occur. It is suggested that this devitrification of the bond accounts for the fact that specimens fired at 1093°C have a lower strength than those fired at 371°C or 815°C. These authors also confirmed that the addition of Cr_2O_3 increases

the thermal stability of the phosphate bond.

Premature hardening of high alumina refractories accompanied by loss of workability is often encountered. This problem is associated with formation of insoluble $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$. Sequestering agents like acetyl acetone, sulfo-salicylic acid, dextrine, oxalic acid and citric acid can be added to stabilize the mix.⁽¹⁶⁾

2.3.2. SODIUM SILICATE⁽¹²⁾

Industrial sodium silicate is a colloidal solution of highly hydrated silica, which is dispersed by the presence of hydrolytic sodium hydroxide. A completely hydrolysed sodium silicate under the action of carbon dioxide in the atmosphere, results in the separation of silica in the form of gel, which then sets by condensation into polysilica structure. On heating, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ melts at 874°C and the combination of this silica with SiO_2 , which lies in the sodium silicate range, appears as eutectic at 790°C . The usefulness of sodium silicate as binding agents in refractory concrete lies in their high reactivity, which enables reactions to take place with a great variety of aggregates, resulting in compounds which are thermally stable and having good fire resistance.

2.3.3. ASHMENT CEMENT

High temperature insulating concretes are made by mixing porous aggregates and portland cement, sodium silicate,

alumina cement, phosphoric acid etc., and casting and curing the same at room temperature. These concretes have many advantages in application. In the case of rice husk ash porous particles, portland cement is the most appropriate type of bond from the point of economy, availability and the ease of use. The hydration and hardening of portland cement are distinguished by two fundamental processes associated with the principal component, tri-calcium silicate: the formation of calcium silicate hydrates, of low lime content compared with the lime-rich clinker minerals, and the resultant occurrence of free lime in the form of hydrated lime, Ca(OH)_2 . The reaction with the crystalline phase of "tobamomite" and having property of retaining water. The surplus lime is deposited in the form of Ca(OH)_2 layer between the crystals of tobamomite. The hydration of aluminates give C_2AH_7 to C_4AH_{13} depending on amount of lime. The most stable one is C_3AH_6 . C_3A and C_3S hydrate most rapidly, C_4AF slowly and C_2S slowest of all. The reaction is accelerated if the temperature is raised (steam treatment, autoclave hardening).⁽¹²⁾

If a portland cement structure is subjected to heating after it has set, the gel water is driven out in the range of 100-200°C and dehydration of Ca(OH)_2 occurs between 500-600°C. At 800°C dewatering of calcium silicate hydrates occur with loss of strength, see Figure 2.3. However, the strength picks up again beyond this temperature range due to formation of ceramic bond.⁽¹²⁾ The presence of free CaO

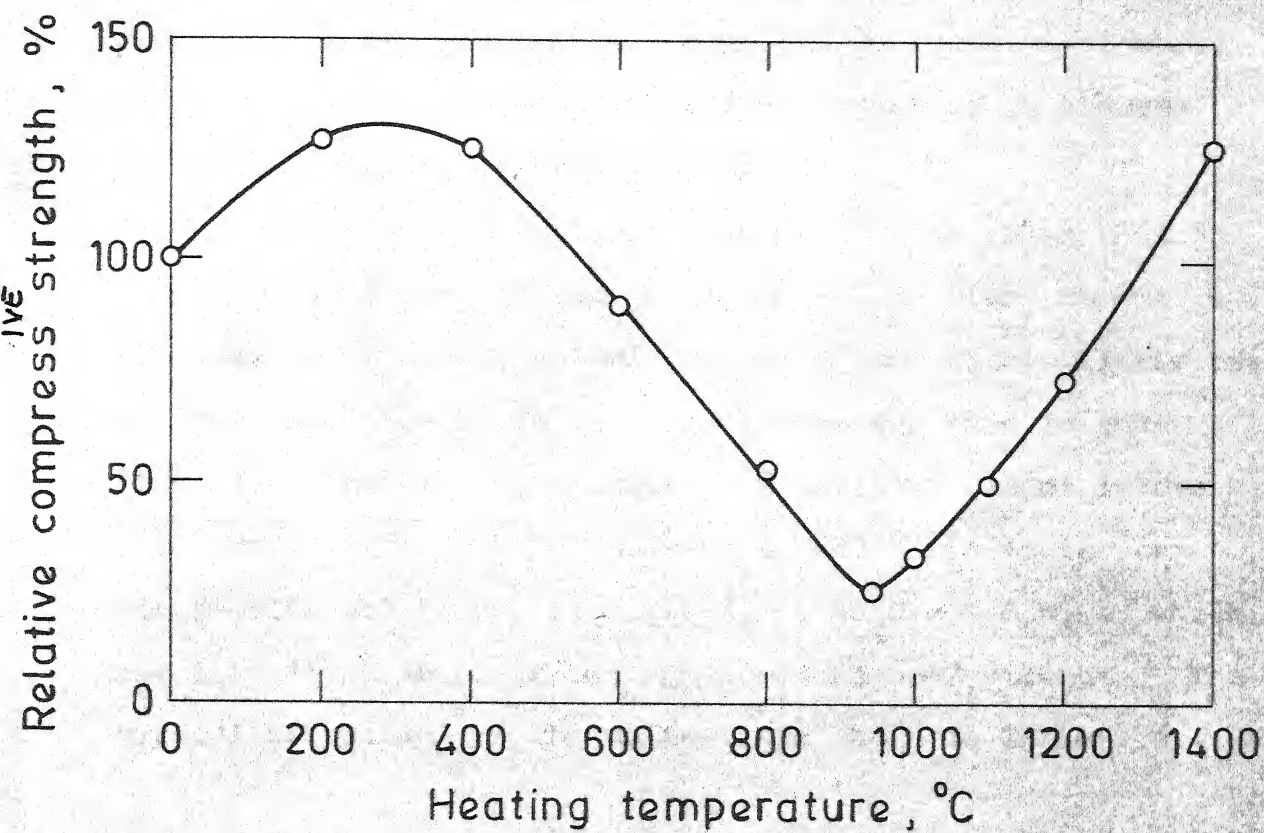


Fig. 2.3 The relative cold compressive strength of portland cement after subjection to heat.

above 600°C denotes a possible source of weakness in portland cement bond, because rehydration will take place on cooling and as a result cracks may be formed leading to damage of the cement structure. This is because, the formation of Ca(OH)_2 from CaO results in a volumetric expansion of about 44%. Owing to this reason, portland cement is considered unsatisfactory as a refractory bond.

Earlier work at I.I.T. Kanpur⁽¹³⁾ has shown that an interground mixture of rice husk ash and portland cement in proportions of 40:60, called "ashment" cement, has little or no free lime present in it. The reason for this is that free lime liberated by hydration of portland cement reacts with ground rice husk ash present in the vicinity to form tobermorite gel ($-\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O} = \text{C}_5\text{S}_6\text{H}_5 -$) which not only fixes the lime but enhances the bond strength. The typical properties of the ashment are shown in Table 2.4.

TABLE 2.4. Compressive Strength (kg/cm^2) of 1:3 Cement Sand Cubes.

Ageing time (Days)	OPC	Ashment (ash/cement = 1:2)
3	113	147
7	150	274
14	186	327
21	235	376
28	277	442
90	342	-

CHAPTER - 3

OBJECTIVES OF THE PRESENT WORK

The underlying objective of this work is to determine the practical feasibility of manufacturing thermal insulations from rice husk ash and thermit slag. The detailed programme is as follows:

- (1) Characterization of thermit slag, including preliminary studies on hydraulic setting properties with and without lime, various phosphate bonds and sodium silicate, and their binding properties.
- (2) Manufacture of thermit slag light weight insulation bricks and bubbles.
- (3) Characterization of rice husk ash, specially the effect of combustion temperature of husk.
- (4) Manufacture of porous mullite insulation bricks.
- (5) Manufacture of hydraulic setting rice husk ash insulation bonded with calcium silicate or ashment cement.

CHAPTER - 4

MATERIALS AND METHODS

4.1. MATERIALS

Materials used in these experiments were rice husk ash, thermit slag, alumina, pop-corn and chemical bonds.

4.1.1. RICE HUSK ASH

Most of the ash used in the experiments was prepared by burning rice husk in the laboratory in TIB (tube-in-basket) furnace designed by Kapur⁽¹⁹⁾ (see Figure 4.1). The burning of husk in the burner is accomplished by two combustion processes that occur simultaneously i.e. by combustion of gassified volatile matter (which constitutes 50-60% of rice husk⁽⁴⁾) at the mouth of the burner tube and direct burning of remaining wood tar and fixed carbon in the husk bed. The ash produced from the furnace was highly reactive amorphous silica, substantially free of carbon.

An attempt was made to characterize the ash ~~subjected~~ at different temperatures for its crystalline nature, surface and physical properties. For these experiments, ash was first prepared by burning small heap of rice husk (150 gm) in nominally constant temperature environment of 350°C. The typical design of the experimental set-up is shown in Figure 4.2. The temperature changes inside the husk bed in the furnace were measured with time. The typical

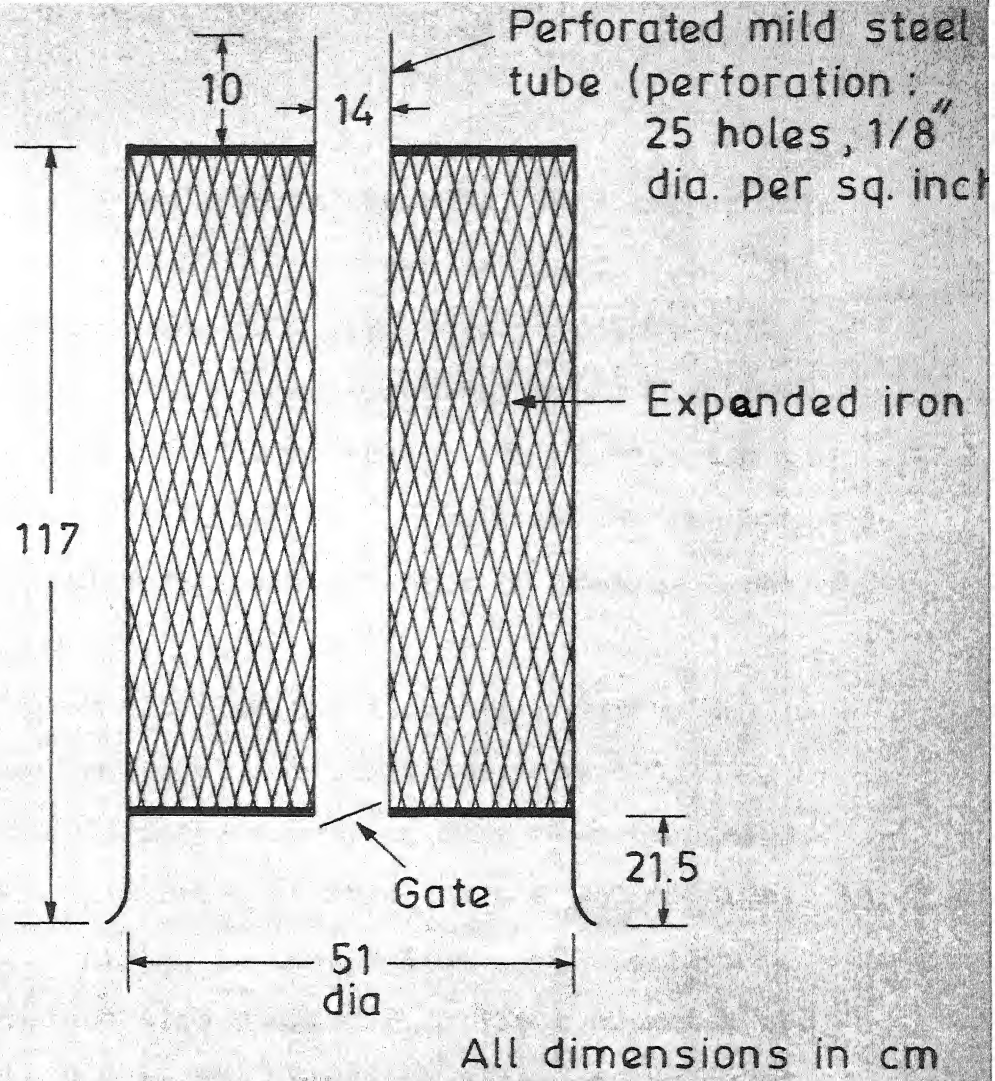


Fig. 4.1- Tube-in-basket furnace.

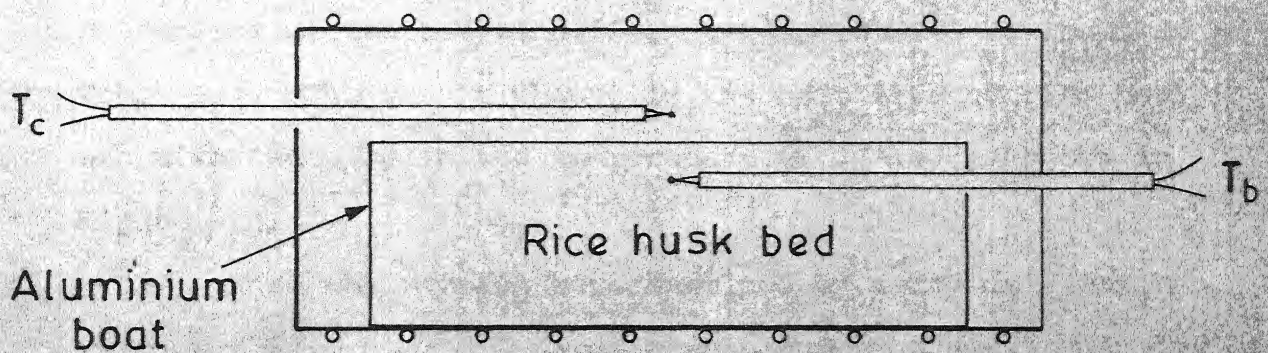


Fig. 4.2- Experimental set up for the constant temperature environment furnace for rice husk burning.

temperature profile with time in the husk, when temperature controller was fixed at 350°C is shown in Figure 4.3. The resultant ash produced was of light brown in colour with little or no carbon. The temperature inside the husk bed T_b shoots up to near 600°C even though the furnace temperature T_c was maintained at 350°C . Hence this was the minimum temperature at which husk could be burnt to produce essentially carbon free ash.

The ash produced from the above procedure was subjected to heat treatment for 10-15 hours at 600, 800, 1000, 1200 and 1400°C respectively in fire clay crucibles. The ash exhibited sintering, starting from 800°C onwards. As the temperature of firing increased from 600°C to 1200°C , the colour of the ash also changed from light brownish red to white probably due to the oxidation state of the multi-valent cation impurities in ash, specially iron. The ash produced at 1400°C showed slight brownish colour because of the reaction of rice husk ash with the fire clay crucible. The colour of the ash at different temperatures is shown in Table 4.1. The weight change in the heat treated rice husk ash with increase in the temperature ($5^{\circ}\text{C}/\text{min}$) is shown in Figure 4.4.

When the samples were examined by X-ray diffraction (Figure 4.5), the 350°C fired sample showed a small quantity of crystalline quartz and the rest was amorphous silica, as opposed to the work of Ibrahim et.al.⁽⁶⁾ who reported no signs of crystalline quartz at any temperature ranges.

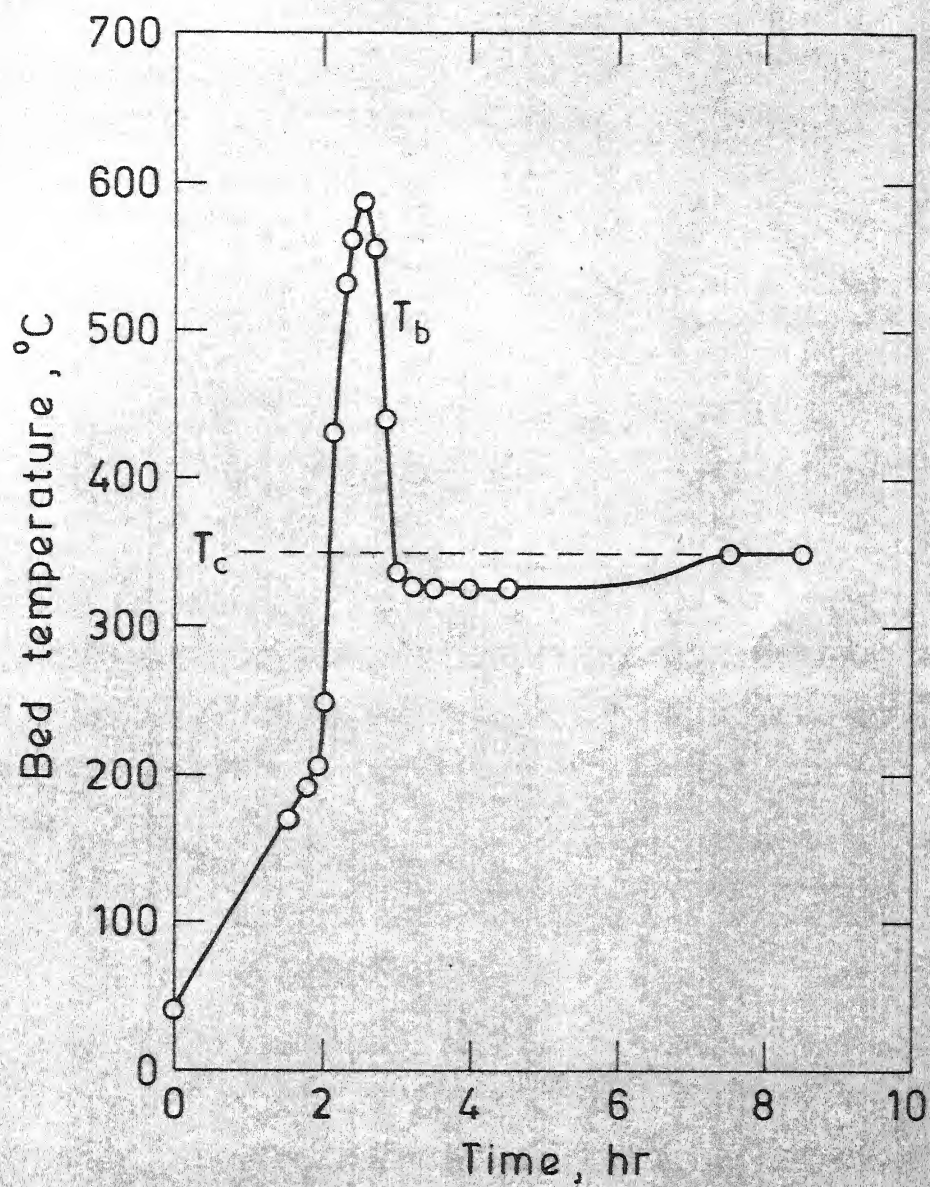


Fig. 4.3 - Temperature variation in the husk bed at constant temperature in environment with time.

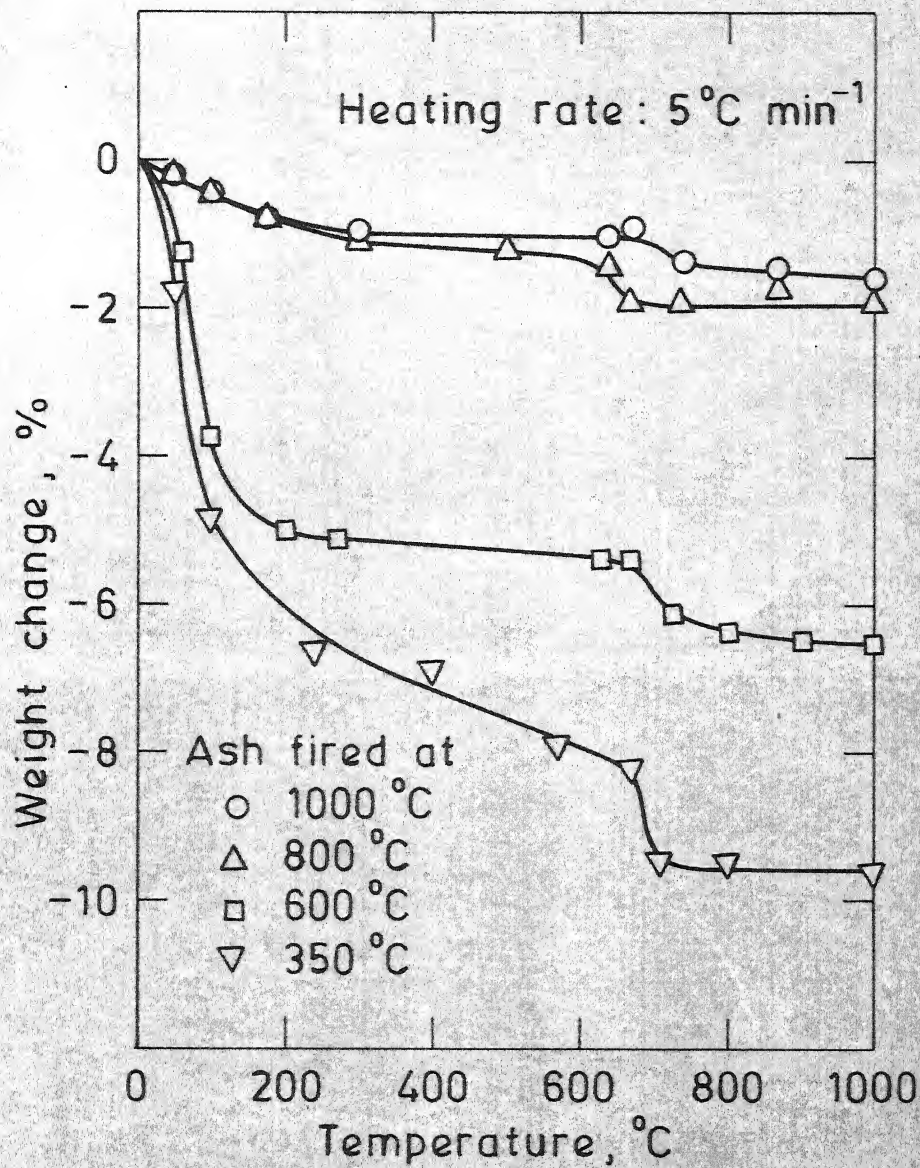


Fig. 4.4 - Thermogravimetric analysis on rice husk ash fired at different temperatures.

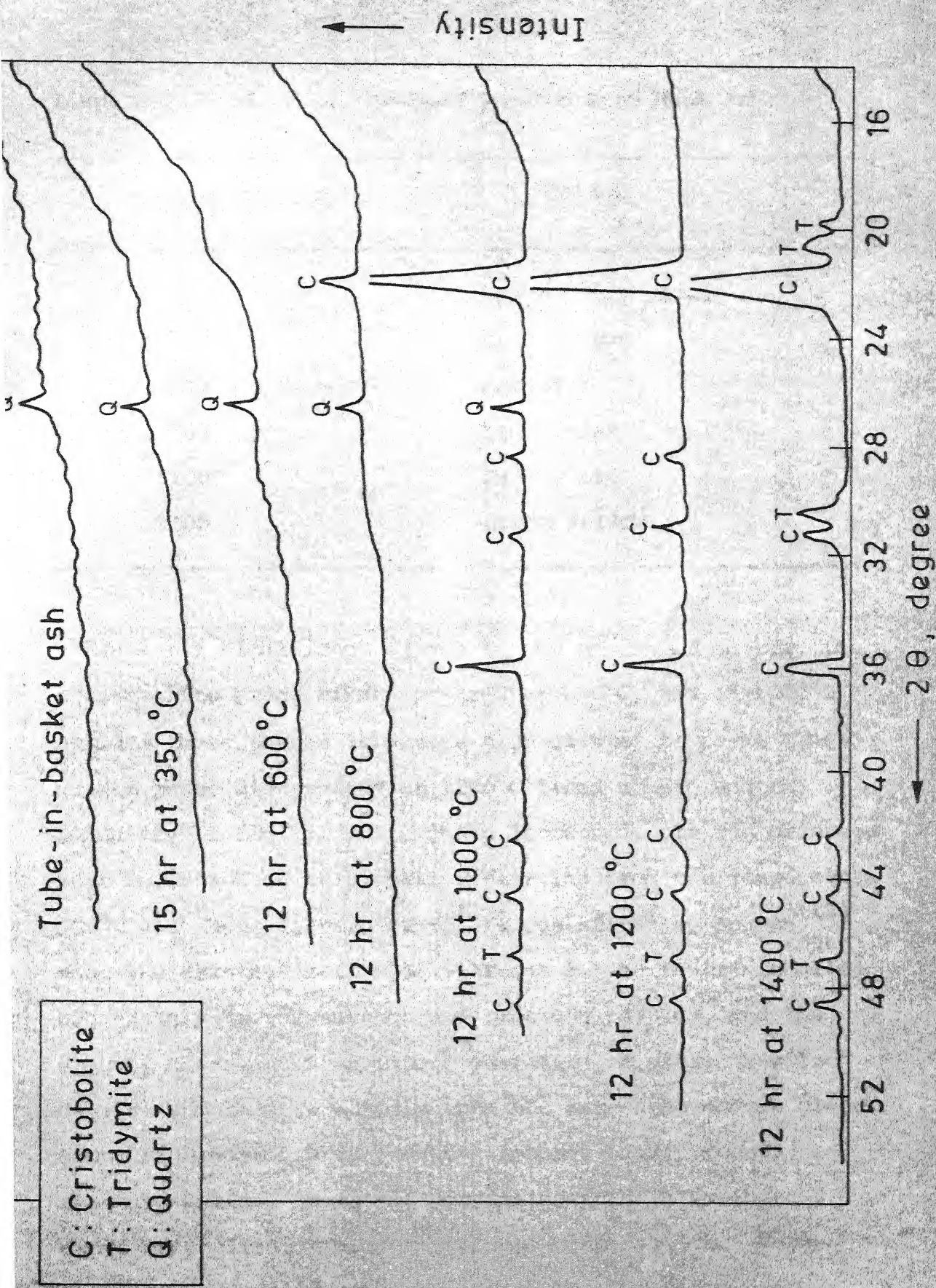


Fig. 4.5. X-ray data on heat treated rice husk ash at different temperatures.

TABLE 4.1. Colour of the Heat Treated Rice Husk Ash.

Temperature °C	Colour
350	Light dirty brown
600	Light brown
800	Red pink
1000	Light pink
1200	Pure white
1400	Light yellow

Without any significant change in the amount of quartz, the cristobalite phase first appeared at 800°C, and at 1000°C besides these phases tridymite also started to form. The quartz phase disappeared at 1200°C fired sample and the intensity of the tridymite phase increased. It was observed that formation of cristobalite starting from the temperature 800°C and above is very fast. It was stated by Sosman⁽¹⁸⁾ that the crystallization of vitreous silica to cristobalite begins only at the surface and proceeds inwards, and the opaque, translucent or impure varieties of vitreous silica devitrify much more rapidly than the pure homogeneous glass. Since rice husk ash is somewhat impure, highly porous, reactive silica, it is not surprising that it exhibits a rapid crystalline transformation to cristobalite. X-ray diffraction data on ash produced in the TIB burner in

Figure 4.5 shows that it is essentially amorphous. This is understandable in view of the fact that the husk bed stays relatively cool in TIB furnace.

The variation of density of rice husk ash with temperature is shown in Figure 4.6. The density results are somewhat erratic because of (1) the presence of small amounts of unburnt carbon trapped in the matrix, (2) the oxidation state of iron is variable, (3) extremely fine enclosed micropores are present, and (4) the density of silica polymorph depends on its thermal history and impurities. However the fact remains that density shows an abrupt increase between 800-1000°C temperatures corresponding to the appearance and development of cristobalite phase in the X-ray data. In the literature the densities (gm/cm^3) of silica polymorphs are given as (1) Quartz: 2.65, (2) Cristobalite = 2.32, (3) Tridymite = 2.26, and (4) Vitreous silica = 2.2.

The ash used in the manufacturing mullite insulations and ashment bonded insulations had the following characteristics:

Bulk density (loose): 0.098 gm/cc

Tap bulk density: 0.25 gm/cc .

4.1.2. THERMIT SLAG

The thermit slag was obtained from M/s. ABM Metalloys Ltd., Shimoga, Karnataka State. The chemical analysis of the slag is given in Table 2.3. The slag was in the form of large lumps. It was subjected to rolls crushing and then to fine grinding. Its typical characteristics are:

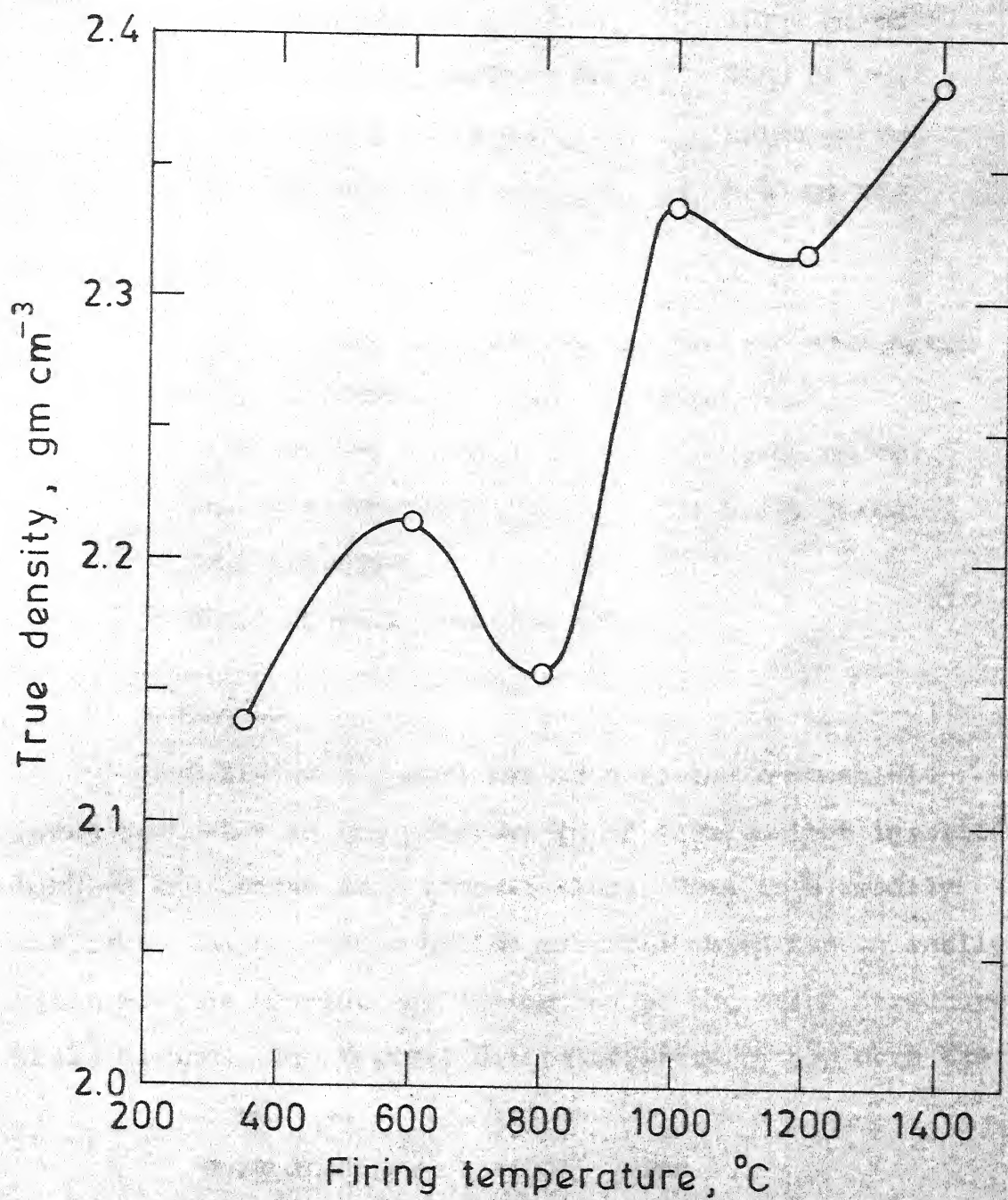


Fig. 4.6 - Variation in true density of rice husk ash with firing temperature.

True density:	3.397 gm/cc
Blain specific surface area:	2900 cm ² /gm
Bulk density (loose):	1.126 gm/cc
Tap bulk density:	1.40 gm/cc.

4.1.3. ALUMINA

Bayers alumina was used in the present work after fine grinding. Its typical characteristics are:

Bulk density (loose):	0.696 gm/cc
Tap bulk density:	0.974 gm/cc
True density:	
Blain specific surface area:	

4.1.4. POP CORN

Exfoliated pop corn was used as the combustible pores generator in the manufacture of light-weight insulation bubbles and bricks from thermit slag. This is a readily available cheap organic hollow material which can be easily burnt without causing any disruption to the brick structure while firing. The typical characteristics of pop corn are:

Size:	5-6 mm
Bulk density:	0.0635 gm/cc
Ash:	1.72%

4.1.5. CHEMICAL BONDS

Initially a number of chemical bonds were tried with thermit slag to obtain preliminary data on strength at room temperature, setting time, as well as strength at higher

temperatures: Phosphoric acid, Di ammonium phosphate, sodium hexa meta phosphate, sodium phosphate, calcium oxide, etc. Out of these bonds, phosphoric acid, Di ammonium phosphate, sodium hexa meta phosphate were considered to be relatively better when compared with the others. The typical properties of the pellets prepared by these bonds with the thermit slag are shown in the Chapter 5.

4.2. METHODS

4.2.1. GRINDING

Ball mill for the grinding of the raw material is of the following specifications:

Height of the ball mill:	21 cm
Internal diameter of the ball mill:	28.5 cm
Volume of the ball mill:	13.61 litres
Revolutions per minute:	60
Outer diameter of the ball mill:	31.81 cm

Amount of the grinding media (alumina ~~cylinders~~) was fixed so as to fill 40% of the ball mill volume. The grinding media specifications are as follows:

Large cylinders - Height:	2.072 cm
Diameter:	2.065 cm
Weight:	10.5 kg.

4.2.2. DISC AND CUBE SAMPLES

Steel rings of 7 cm internal diameter and 3.5 cm height were used as moulds to make discs of hand compacted

samples; besides a die and punch mould of 5 cm internal diameter was used for pressing on a hydraulic press at 115.5 kg/cm^2 pressure. These discs were used to determine tensile strength by cylinder splitting test (Brazilian test). Standard cast iron moulds of face area 25 cm^2 were used to make cube samples.

4.2.3. MIXING PROCEDURE

In producing thermal insulation using thermit slag, the mixing of the ground thermit slag and the dilute phosphoric acid was done quickly so as to eliminate premature and localized setting of the mixture. The particle size distribution of the slag and concentration of the phosphoric acid are the two parameters which determine the rate of reaction and subsequent setting of the mix. A small quantity of fireclay (about 5%) was added to slag for better plasticity to the mix and well sintered brick after firing. The mix was hand moulded in a ring mould, with its internal surface covered with oiled paper to facilitate easy stripping after hardening.

In case of ashment bonded bricks and mullite insulations, it was found that rice husk ash had to be free from unburnt husk, failing which lamination cracks appeared in the machine pressed cured discs, but not so in the case of hand moulded samples. This could be due to expansion of husk on absorption of water during the curing treatment.

In the case of machine pressed mullite insulation and ashment

bonded rice husk ash, for every 50 gm of mixture 15 ml of water was added, and in the case of hand moulded insulations 65 ml of water added for 125 gm of the mixture.

4.2.4. HARDENING AND CURING

Thermit slag insulating discs and cubes were subjected to curing-cum-hardening procedure at 1150°C for 2 hours in an oven. The ashment bonded rice husk ash discs and cubes were air dried for 24 hours at room temperature and then subjected to steam curing for 4 hours at the steam pressure of 1.5 atmospheres in a pressure cooker.

4.3. TESTING

4.3.1. POROSITY

For determination of porosity of a sample, Archimedis liquid displacement technique was adopted.

After weighing the dry test piece, it was boiled in the water for 1 hour to make liquid penetrate into the pores of the sample.

$$\text{Percentage apparent porosity: } P = \frac{W_c - W_a}{W_c - W_b} \times 100$$

W_a : weight of the dry test sample

W_b : weight of the test piece soaked with water and suspended in water

W_c : weight of the test piece soaked with water and suspended in air.

Besides, other tests like determination of Apparent density, Tap density, True density, Blain specific surface area, Splitting test, Cube compression test were done on the samples.⁽¹¹⁾

4.3.2. X-RAY DIFFRACTION

X-ray diffraction was done on the heat treated rice husk ash and mullite samples to determine the possible phases present. The experiments were conducted on the General Electric XRD-5 machine. The experimental parameters were kept constant for any particular material, which are shown in the Table 4.2.

TABLE 4.2. Experimental Parameters for XRD-5.

Parameters	Rice husk ash	Mullite
Target	Copper	Copper
Radiation (\AA)	K (1.5405)	K (1.5405)
Filter	Nickel	Nickel
Scanning range	15 - 55°	15 - 80°
Counts per second	1000	1000
Scanning speed (°/minute)	2	2
Slit width	3°	3°
Target voltage (KV)	30	35
Target current (mA)	12	11

CHAPTER - 5

PRELIMINARY TRIALS

Preliminary trials were made on thermit slag to choose an appropriate bond which is (1) a relatively cheap chemical, (2) of low initial setting rates and (3) capable of giving good strength properties at high temperatures.

The ground slag was mixed with different bonds, ⁽¹⁴⁾ pellets were formed by hand rolling. After curing for a day or two in air, the relative strength was ascertained in a quantitative manner either by dropping them on floor from a fixed height or by the scratch method. The typical properties of these pellets at room temperature are shown in Table 5.1.

The cured pellets (balls) were heated to different temperatures and again subjected to quantitative tests for the strength. The results are shown in Table 5.2. It was therefore decided to select 40% phosphoric acid as the bond for further work, as well as with sodium silicate bond which is a standard bond in high temperature refractories.

Table 5.1. Setting Time and Relative Strengths for Ground Thermit Slag with Different Chemical Bonds at Room Temperature.

Type of Bond	Mixing Proportion	Setting Time (minutes)	Relative Strength
Di ammonium phosphate(s)	13%	Too slow; 20 minutes	Very high (hard)
Sodium hexa meta phosphate(s)	13%	Considerably fast when compared to Di ammonium phosphate	Very high
Sodium phosphate(s)	13%	- do -	Low
Calcium oxide(s)	5%	- do -	Very high
50% phosphoric acid solution	15 ml for 100 gms slag	Very fast: 2-3 minutes	Very high
25% phosphoric acid solution	- do -	Slow: 35 minutes	Medium
100% phosphoric acid solution	- do -	Very slow	Low
Water	--	--	Low strength

Table 5.2. Relative Strength of Thermit Slag with Different Chemical Bonds,
Fired to Different Temperatures.

Binder/Amount	Colour/Strength					Comments
	Firing Temperature (°C)					
	Room Temp.	100	200	400	600	
Di ammonium phosphate(s) (13%)	Brown/Good	Yellow/Good	Yellow/Good	Brown/Good	Brown/Good	Satisfactory
Phosphoric acid (sol) (10% and 25%)	Yellow/Poor	Yellow/Poor	Yellow/Poor	Light Brown/Poor	Light Brown/Poor	Unsatisfactory
Phosphoric acid (sol) 50%	Brown/Good	Brown/Good	Brown/Good	Brown/Good	Dark Brown/Good	Satisfactory
sodium hexa meta phosphate(s) (5, 10 and 13%)	Yellow/Good	Yellow/Good	Yellow/Good	Brown/Good	Dark Brown/Good	Satisfactory
Calcium oxide(s) (10 and 25%)	Yellow/Good	Yellow/Good	Yellow/Poor (Cracked)	Grey/Poor (Cracked)	Dark Grey/Poor (Cracked)	Unsatisfactory
sodium phosphate(s) 13%	Yellow/Poor	Yellow/Poor	Yellow/Poor	Brown/Poor	Dark Brown/Poor	Unsatisfactory

CHAPTER - 6

RESULTS AND DISCUSSIONS

6.1. LIGHT WEIGHT THERMAL INSULATION MATERIALS FROM THERMIT SLAG

Exfoliated pop corn was used as porosity inducer in case of thermit slag light weight insulations. These insulation bricks were prepared using chemical bonds - Sodium silicate and Phosphoric acid.

6.1.1. SODIUM SILICATE BONDED THERMAL INSULATIONS

In the present experimental scheme, varying amounts of slag to pop corn ratios (Z) were tried with sodium silicate solution of specific gravity 1.3. The variation in the bulk densities of the brick fired at 850°C as a function of Z is shown in the Figure 6.1. and Table A1 in Appendix 1. The fired samples at the light end of the bulk density spectrum tend to be friable. It was then decided to try phosphoric acid bond.

6.1.2. PHOSPHORIC ACID BONDED THERMAL INSULATION

Dilute phosphoric acid of varying concentrations (volume %) 40, 30 and 20 were tried with ground thermit slag with three ratios of ^{Z=}1.0, 1.25 and 1.5. Preliminary trials showed that out of these compositions, with 40% phosphoric acid concentration and 1.5 Z gave optimum results with respect to both strength and lightness. These

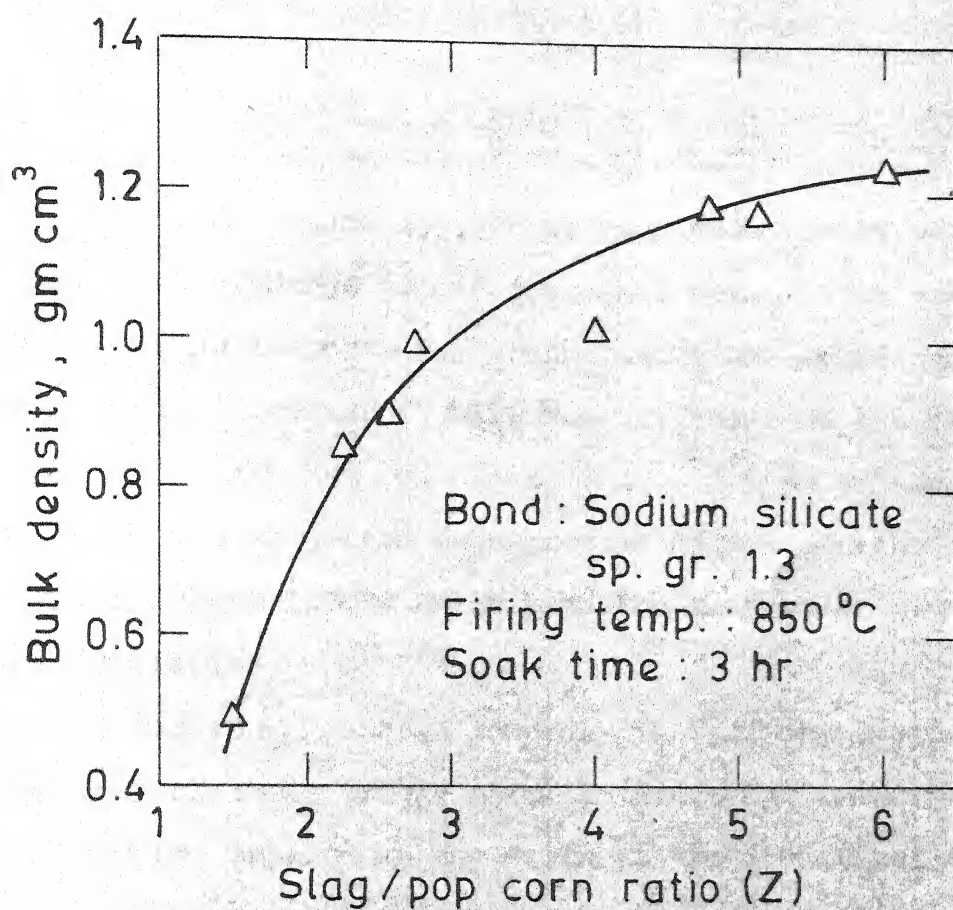


Fig. 6.1.1- Variation of bulk density as a function of slag/pop corn ratio

bricks were prefired to 800°C for 4 hours and then they were subjected to high temperature firing at 1000, 1100, 1200 and 1300°C in order to determine shrinkage behaviour.

6.1.2.1. THE EFFECT OF TEMPERATURE ON SHRINKAGE (LINEAR AND VOLUMETRIC), BULK DENSITY AND STRENGTH

From Figure 6.1.2 it is seen that linear and volumetric shrinkage values increased drastically above 1200°C firing temperature. This result was confirmed by a rather sharp increase in bulk density value of the brick above 1200°C as shown in Figure 6.1.2. It would seem that the brick was subjected to a greater degree of liquid phase sintering above 1200°C which resulted in partial closing up of the pores.

Figure 6.1.3 shows compressive load/deformation behaviour of these bricks fired to different temperatures. The load was applied on the discs in the transverse direction at the rate of 0.5 mm/minute in Instron machine. The samples underwent a gradual compression till 25%, then followed by a sharp failure. In general, the lowest temperature fired bricks showed maximum deformation at any given load. The shape of these curves indicates that initially the load is sustained by the pore walls, followed by rapid collapse of the pores in approximately 5 to 25% deformation range.

From these results, it is concluded that it is possible to make ultralight thermal insulating refractories. Bricks prefired to 800°C can be used upto 1100°C. For increasing the strength and for application at still higher

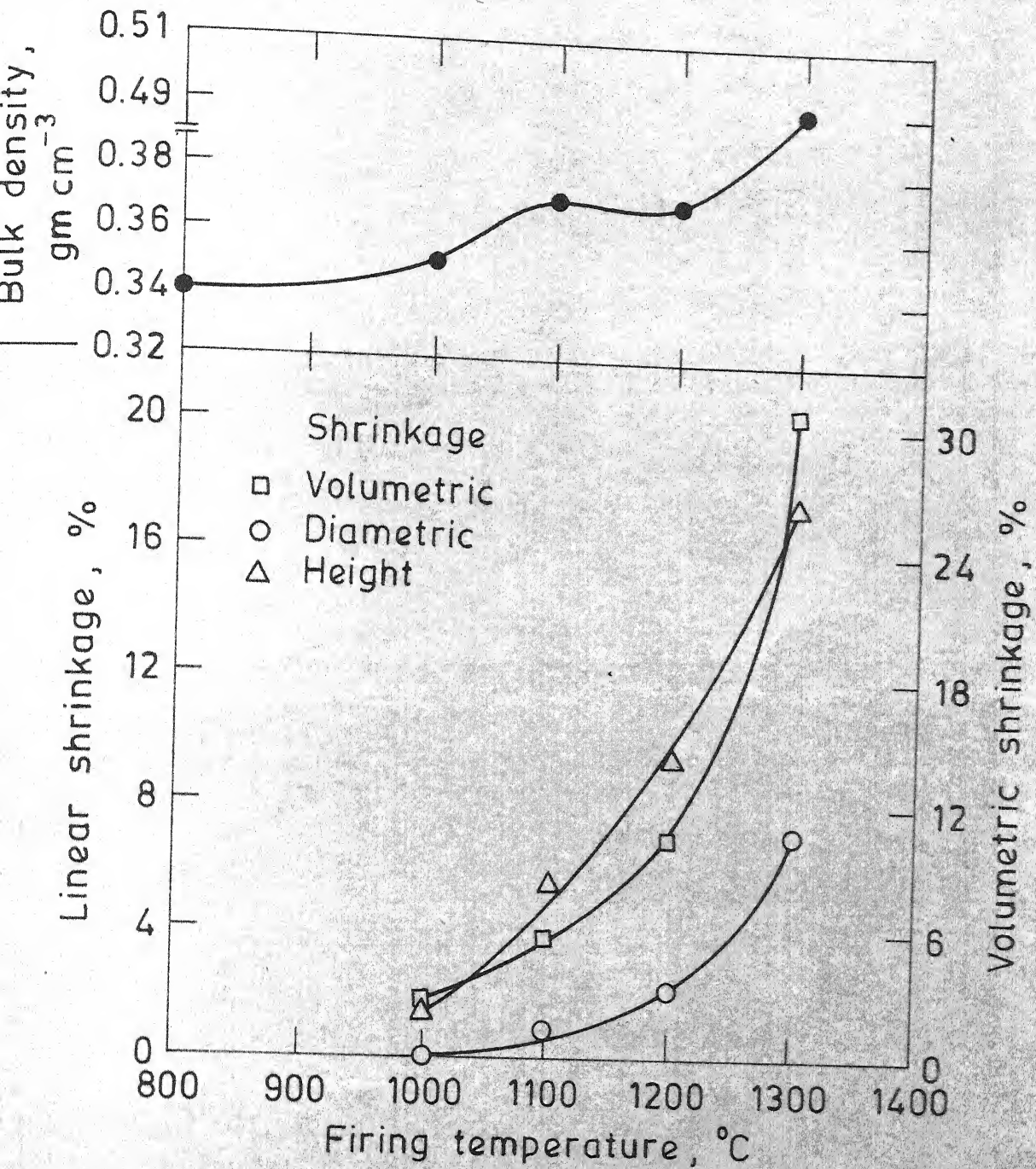
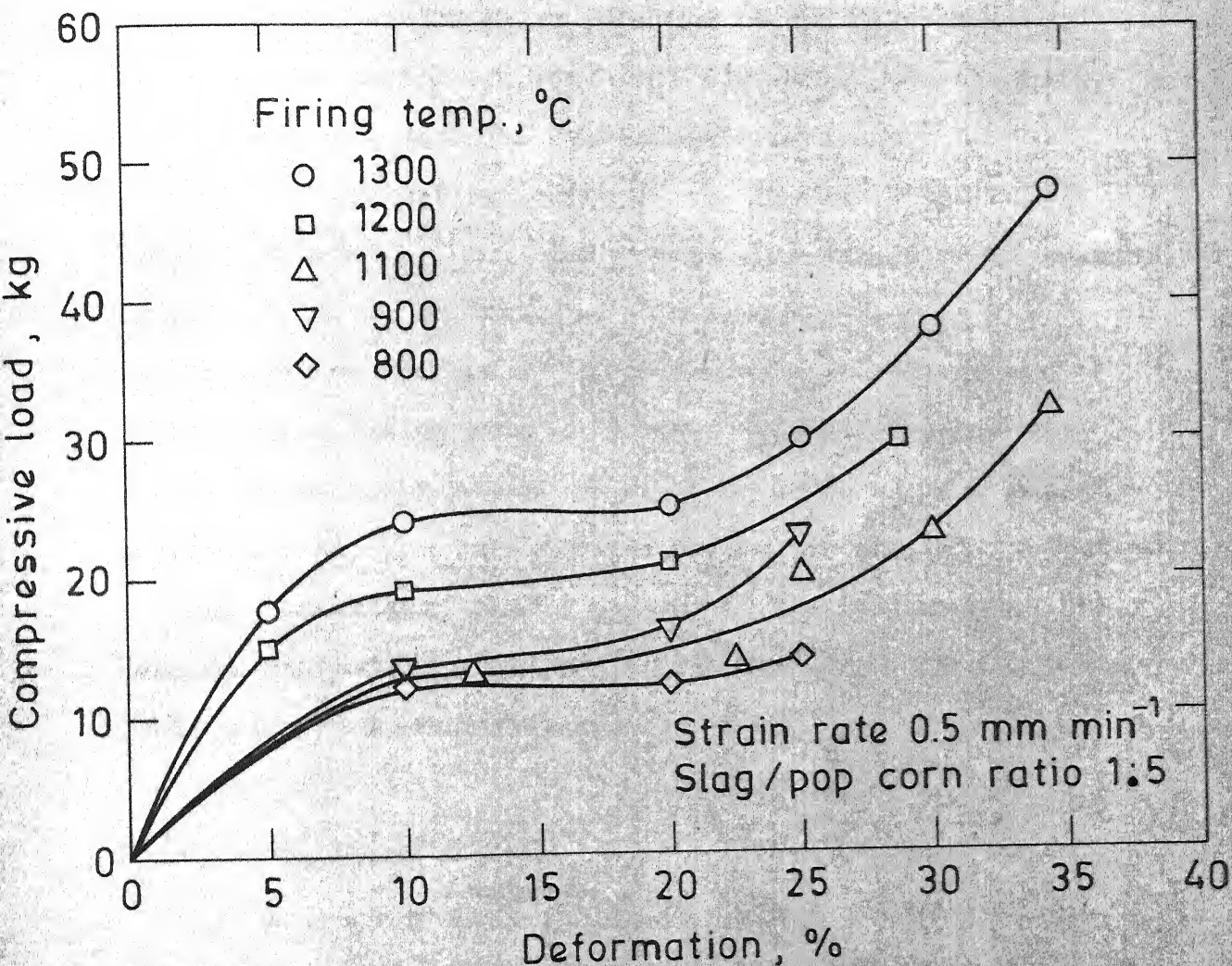


Fig. 6.1.2 Effect of firing temperature on shrinkage and bulk density of phosphate bonded light weight insulation discs.



6.1.3- Variation of compressive load with deformation for phosphoric acid bonded thermit slag light weight insulation disc fired to various temperature.

temperature (e.g. 1300°C), it is necessary to prefire the bricks at correspondingly higher temperatures and some penalty must be paid ~~in~~ an increase in the bulk density. It should be noted, however, that even at 1200°C the bulk density of 0.37 gm/cc is extraordinarily light.

The typical variation of the shrinkage and bulk density values ~~for~~ high temperature fired (discs) bricks are shown in Table A2 in Appendix 1.

Hollow spheres or bubbles were also made from thermit slag, using both phosphoric acid and sodium silicate. These bubbles were prefired to 800°C to burn out the base material, pop corn and the hollow spheres were subjected to high temperature firing to enhance their strength. The typical compositions and their bulk densities are shown in Table A3 in Appendix 1.

6.2. MULLITE INSULATIONS

In many respects ^{mullite, a} material of high refractoriness, excellent thermal shock resistance, high RUL etc., would be an ideal refractory for high temperature thermal insulations. In the present work stoichiometric proportions of alumina and silica in the form of rice husk ash was used. The ash provided not only a reactive silica but also high porosity in the fired brick. The compositions are shown in Table 6.1.

TABLE 6.1. Compositions of Mullite Mixture.

		Code		
		CM	FM	3PFM
Rice husk ash (%) (unground)	75	-	-	
Rice husk ash (%) (ground)	-	75	75	
Bayers alumina (%) (ground)	28	28	28	
Bond	5% dextrine	5% dextrine	30% phosphoric acid	

The green mix was pressed into 5 cm dia and 2.5-3.0 cm high discs under 115.5 kg/cm^2 pressure. All the samples were fired to 1450°C for varying times from 2 hours to 34 hours and tested for shrinkage, porosity and strength.

X-ray diffraction technique was used to identify the formation of mullite in the samples with different soaking times. It was observed that mullite formation was observed in the samples with soaking time of 4 hours at 1450°C (see Figure 6.2). It was observed, some unreacted alumina is also with mullite. As the time of soak at 1450°C increased, the mullite content in the samples was increased.

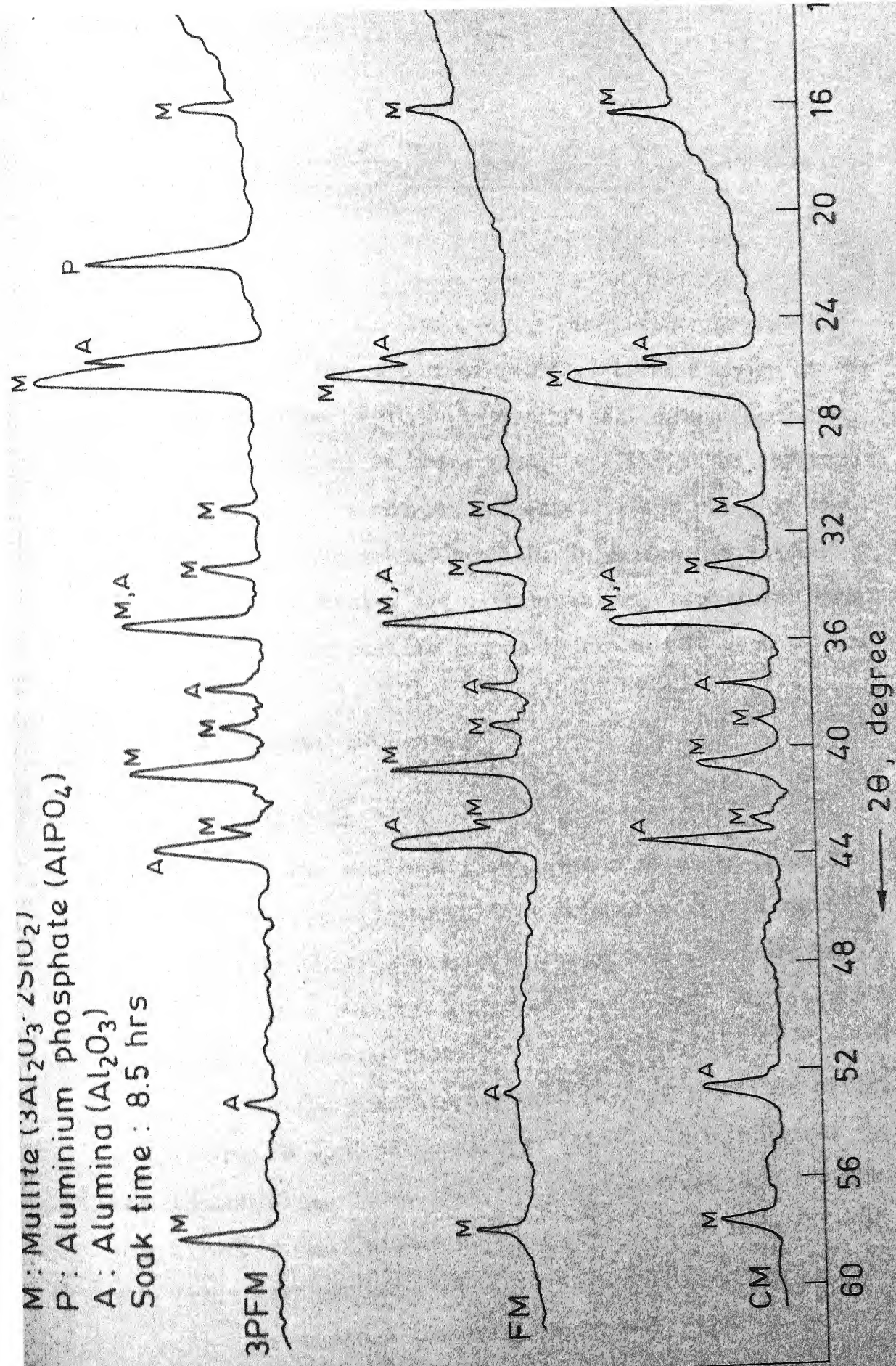


Fig. 6.2. X-ray data on mullite insulation fired at 1450°C with time.

6.2.1. EFFECT OF SOAK TIME AT 1450°C ON THE SHRINKAGE, POROSITY AND TENSILE STRENGTH OF MULLITE INSULATING BRICKS

6.2.1.1. SHRINKAGE

As shown in Figure 6.2.1 the brick underwent 5-8% shrinkage from the green stage to first 8 hours of the soak, after which hardly 0.5% dimensional change occurred after an additional 26 hours soak. The shrinkage represents a sum total of many complex processes taking place in the brick, e.g., phase transformations in silica, shrinkage of pores in ash particles and mullitization. From these results we can infer that mullite porous bricks can be used at temperatures as high as 1500°C without the danger of significant permanent dimensional change.

6.2.1.2. POROSITY

It was observed that porosity level of unground rice husk ash containing mullite samples exhibited more porosity than mullite samples using ground rice husk ash with or without 30% phosphoric acid solution. Porosity data in Figure 6.2.1 shows that:

(1) the porosity was more or less invariant during 8 to 34 hours span of soaking at 1450°C. This confirms the conclusion drawn above that the fired mullite porous bricks are dimensionally stable when exposed to high temperatures for prolonged periods.

(2) whereas the bricks made from ground rice husk ash had porosity in range 51 to 52%, unground ash based

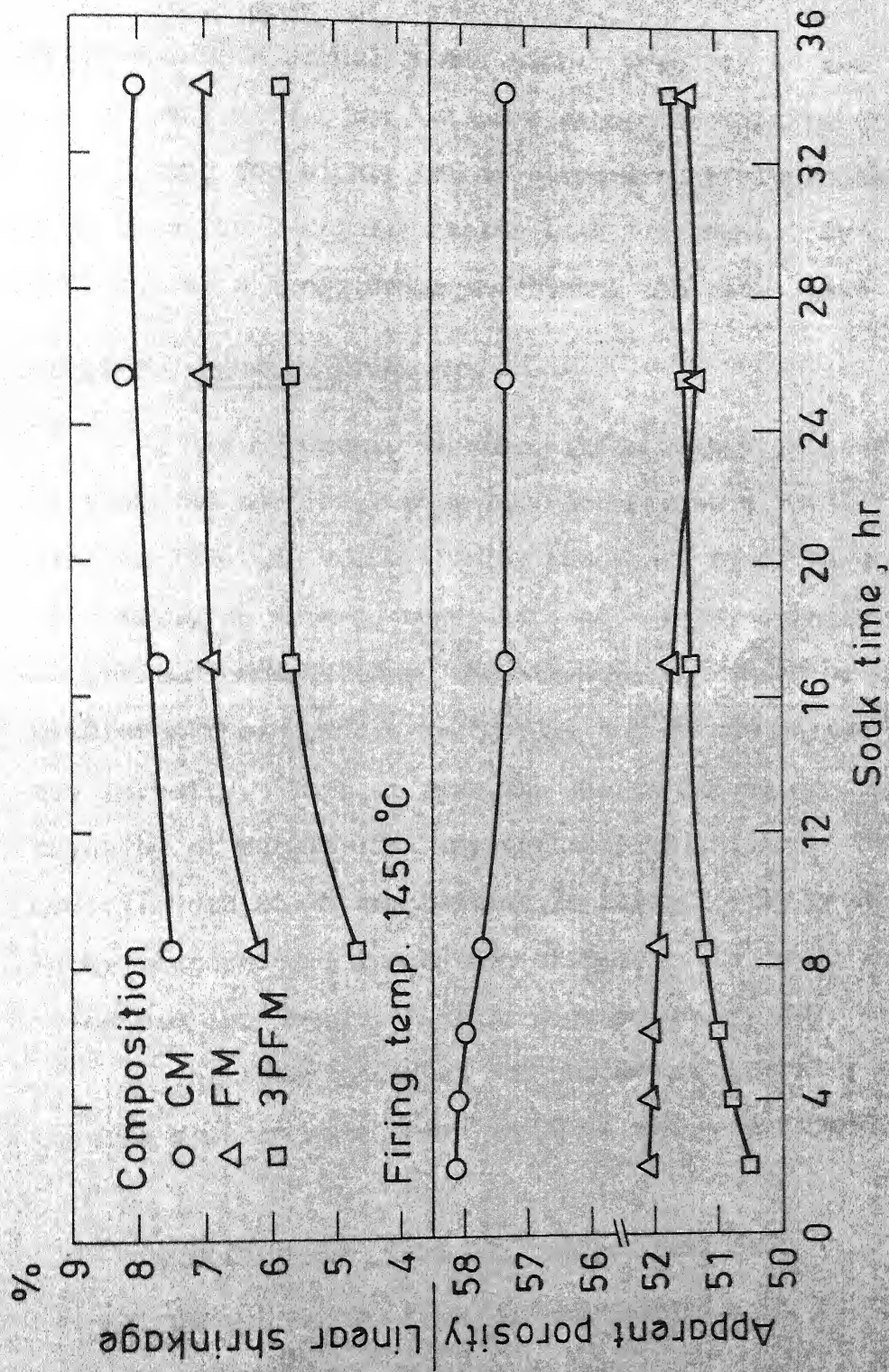


Fig. 6.2.1- Variation of shrinkage and porosity as a function of soak time for mullite insulation discs.

brick showed a significantly higher porosity at about 57%. The primary reason for this difference is that in the course of grinding the highly porous structure of rice husk ash particles are partially broken with attendant loss of void spaces. As a consequence the ground ash packs more densely.

6.2.1.3. TENSILE STRENGTH

As expected, CM composition with highest porosity also showed the least strength (see Figure 6.2.2). In the case of fine ash compositions, phosphate bond was not so effective, as when no bond was used. Interestingly, in the latter two compositions, the strength increased with the time even though there was hardly any change in the shrinkage and porosity. This is possibly due to growth and inter twinning of needle-like crystallites of mullite. Note that the strength of FM composition is sufficiently high to permit incorporation of a few % combustibles (e.g. coke) in the green mix for obtaining still high porosity, say, 60-65%.

The numerical data for shrinkage, porosity and tensile strength are shown in Table A4 in Appendix 1.

6.3. ASHMENT BONDED RICE HUSK ASH INSULATIONS

Unground rice husk ash was bonded with 20, 30 and 40% ashment cement. Insulation cubes and discs were prepared by hand moulding and by hydraulic pressing (115.5 kg/cm^2 pressure) respectively. After air drying and steam curing for 4 hours these samples were subjected to high temperature

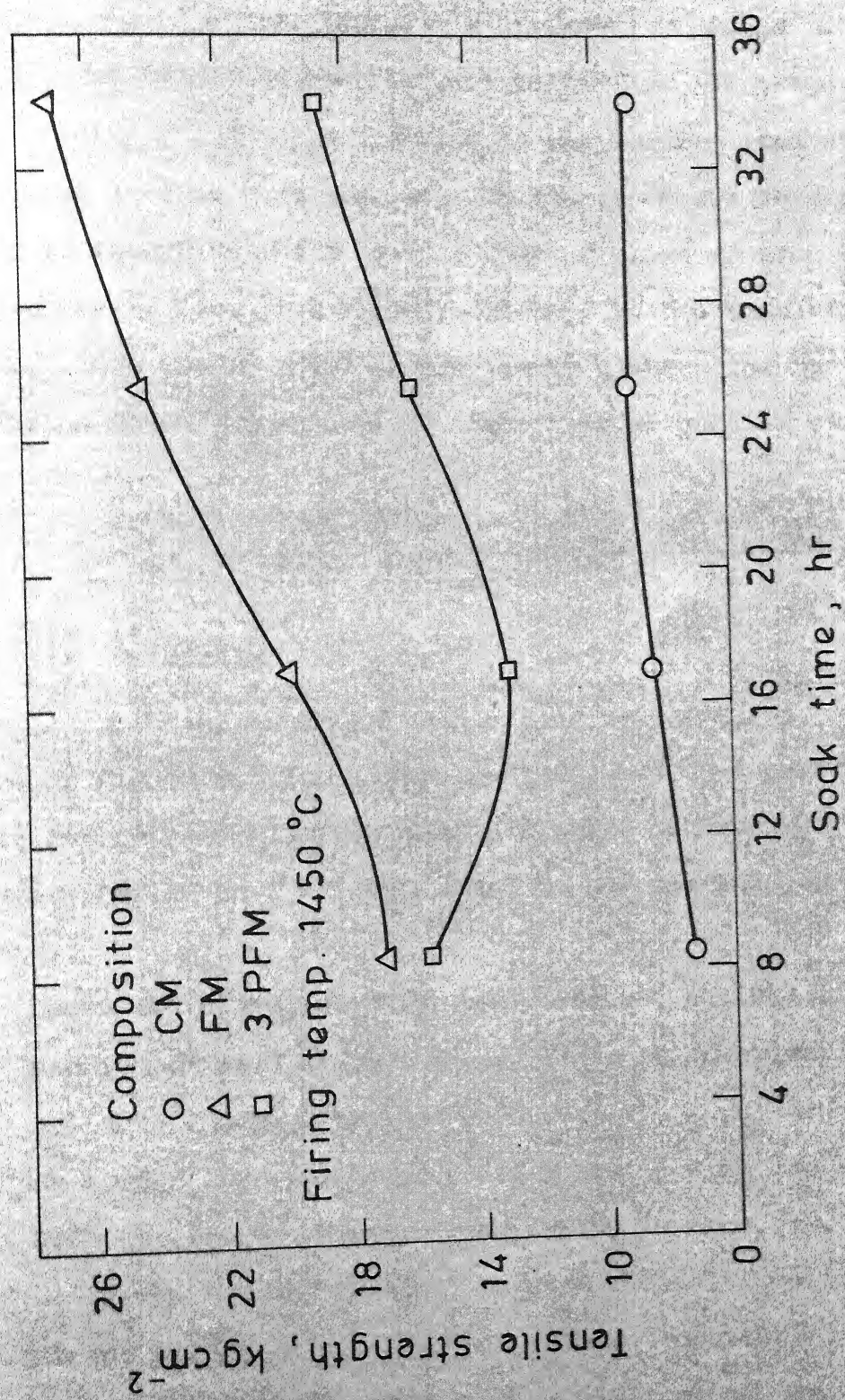


Fig. 6.2.2- Variation of tensile strength as a function of soak time for mullite insulation discs.

treatment for 3 hours, from 200°C to 1200°C in steps of 200°C. The resultant samples were tested for shrinkage, bulk density and tensile strength or compressive strength. The fired samples were also left in the air for 3 days in order to determine the extent of moisture pick-up from the atmosphere by free lime present, if any, in the insulation brick. This was to check if the bricks would crack by expansion which accompanies the hydration of calcium oxide.

6.3.1. THE EFFECT OF TEMPERATURE AND AMOUNT OF BOND ON SHRINKAGE, STRENGTH, HYDRATION AND BULK DENSITY OF ASHMENT BONDED INSULATION BRICKS

6.3.1.1. SHRINKAGE

Linear shrinkages with firing temperatures are shown in Figure 6.3.1 for hand moulded cubes, and in Figure 6.3.2 for machine pressed discs. In spite of somewhat erratic results in the former case, we may conclude that in general:

- (1) Lower the cement content, lower was the shrinkage.
- (2) Machine pressed samples showed somewhat lower shrinkage than the hand moulded ones.
- (3) At 1000°C, the shrinkage did not exceed 2.5% and at 800°C it did not exceed 1.5%, except in one case.

In the case of non-load bearing thermal insulations, a permanent linear change of about 1.5% is acceptable. It then follows that these compositions hold promise, as exceptionally cheap and simple cold setting, cold face

thermal insulations, provided of course the drop in the strength which would accompany the breakdown of hydraulic cement bond in its first heating is not so severe as to disintegrate the structure.

6.3.1.2. STRENGTH

The strength data at different temperatures is shown in Figure 6.3.1 for hand moulded cubes and in Figure 6.3.2 for pressed discs. The drop in strength occurred in 200 to 600°C range, as also reported in the literature, due to breakdown of cement gels with liberation of steam. Permanent ceramic bonding took over beyond 600°C and the strength increased again. Due to better interlocking of particles in machine pressed samples the drop in strength exhibited a mild shallow pattern as compared to more drastic reduction shown by hand mould cubes. However, even in the worst case, the strength values turned out to be adequate for the insulating structure to survive the first heating.

6.3.1.3. HYDRATION

Still another requirement is that, there should not be excessive amount of free lime present in the structure, otherwise expansion cracking may occur due to hydration of lime by the moisture in the atmosphere. Figure 6.3.3 shows the increase in weight when cubes fired to different temperatures were kept in air for 3 days in high monsoon season (humidity around 80%). Part of the weight

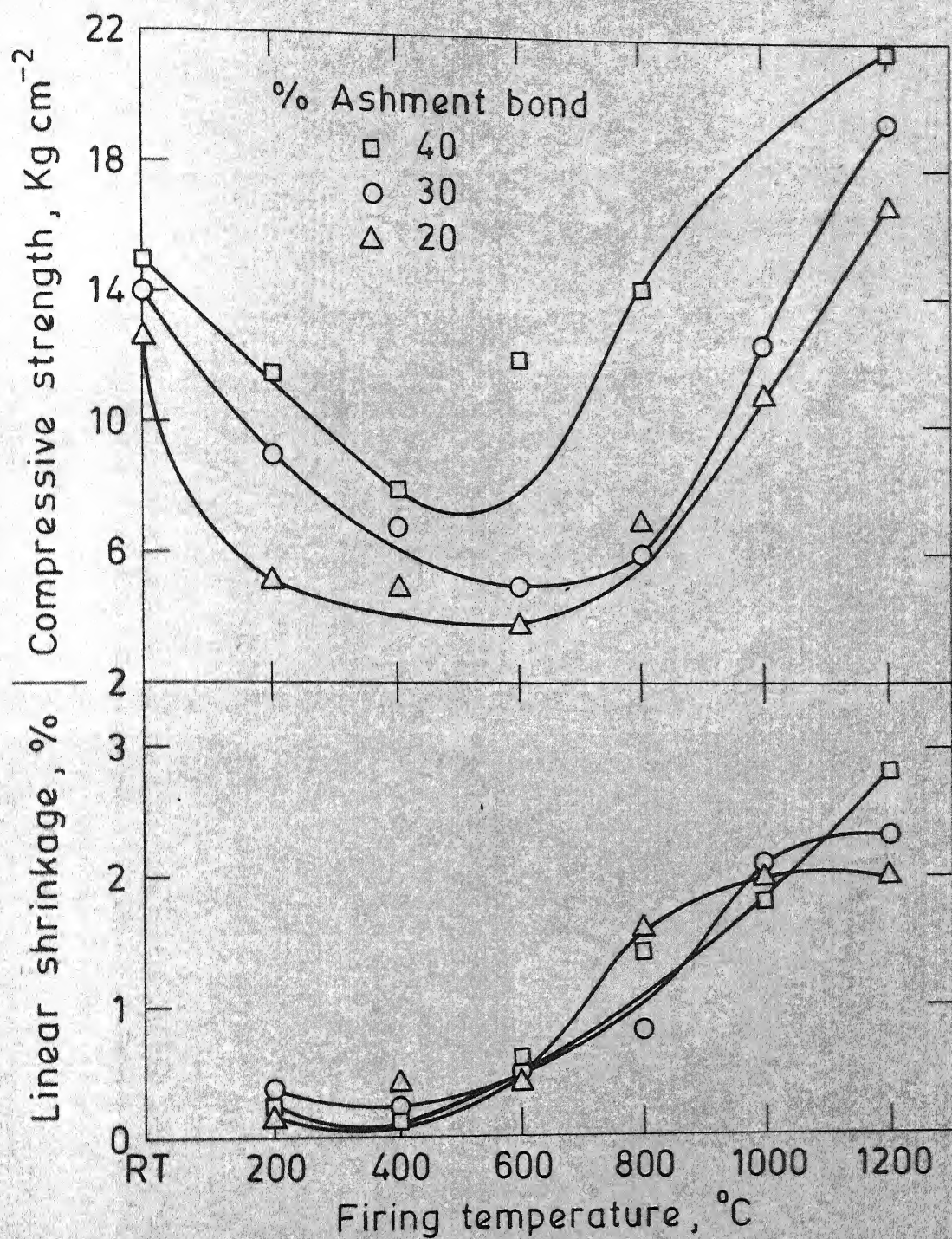


Fig. 6.3.1- Variation of shrinkage and compressive strength as a function of temperature for hand moulded ashment bonded rice husk ash insulation cubes.

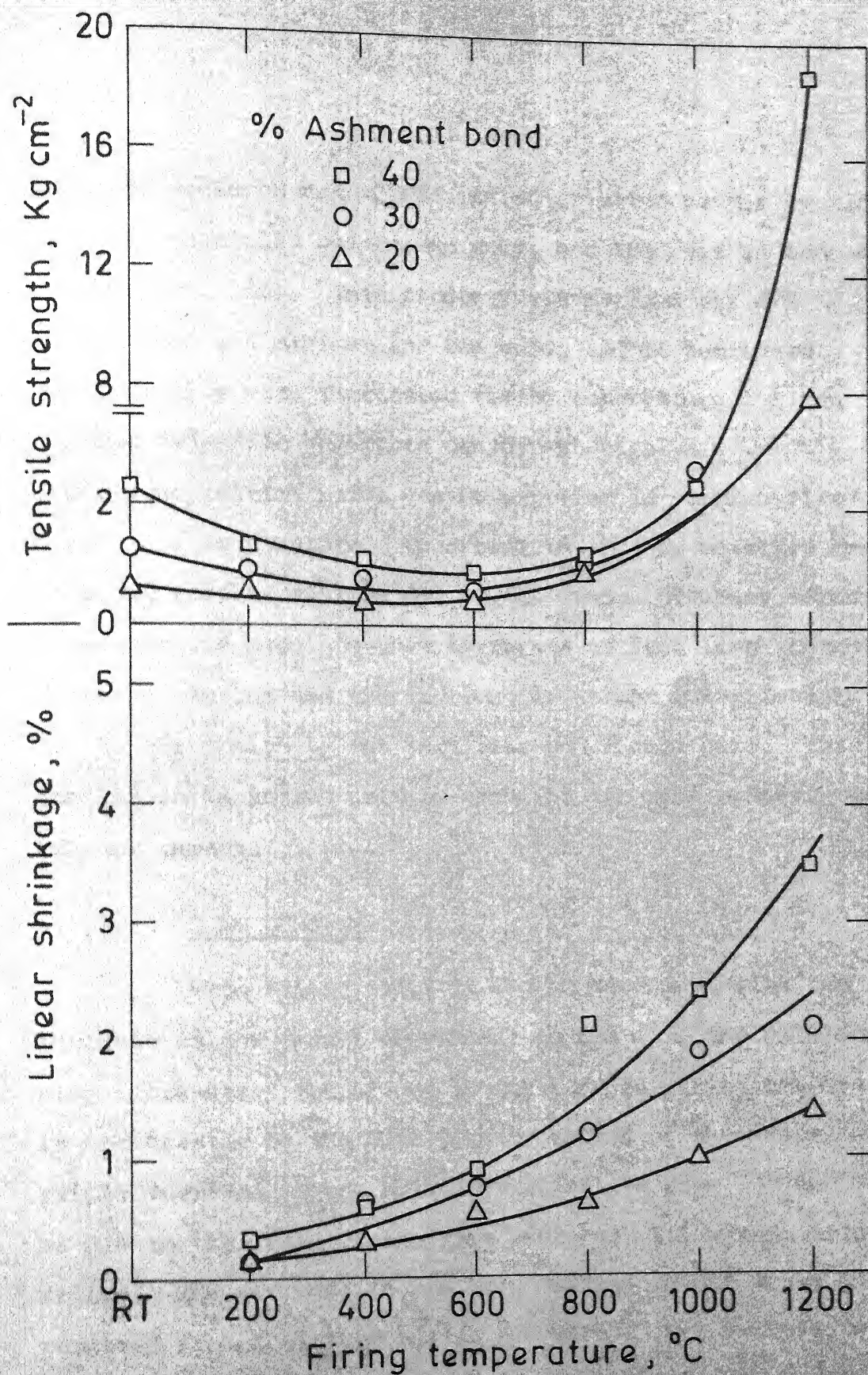


Fig. 6.3.2- Variation of shrinkage and tensile strength as a function of temperature for machine pressed ashment bonded rice husk ash insulation discs.

increase would be due to absorption of water vapour by rice husk ash particles and cement gels, and the rest on account of some free lime. This tendency was maximum for 40% cement bond and minimum for 20% bond, and it decreased monotonically with increasing firing temperature. Since calcium hydroxide undergoes dehydroxylation at 400-500°C, clearly no calcium oxide can be expected in samples fired below this temperature. Therefore the higher moisture content in these samples must be due to adsorption of water vapours. This strongly suggests that there was no free lime present in these samples and the increase in weight was primarily due to adsorption by ash particles and cement gels. This conclusion is in concurrence with the inherent property of ashment cement.

6.3.1.4. BULK DENSITY

From Figure 6.3.3 it can be seen that with the increase in the amount of ashment in the mix, the bulk density also increases. The effect of increase in firing temperature is not drastic on the bulk density values of the discs. The slight decrease in the bulk density values from 200-600°C may be due to the loss of free lime reacting with surrounding silica. The increase in the bulk density values above 600°C resulted from the sintering of the disc. For example, a brick with 40% ashment bond fired at 1200°C for 3 hours has a bulk density of 0.969 gm/cc.

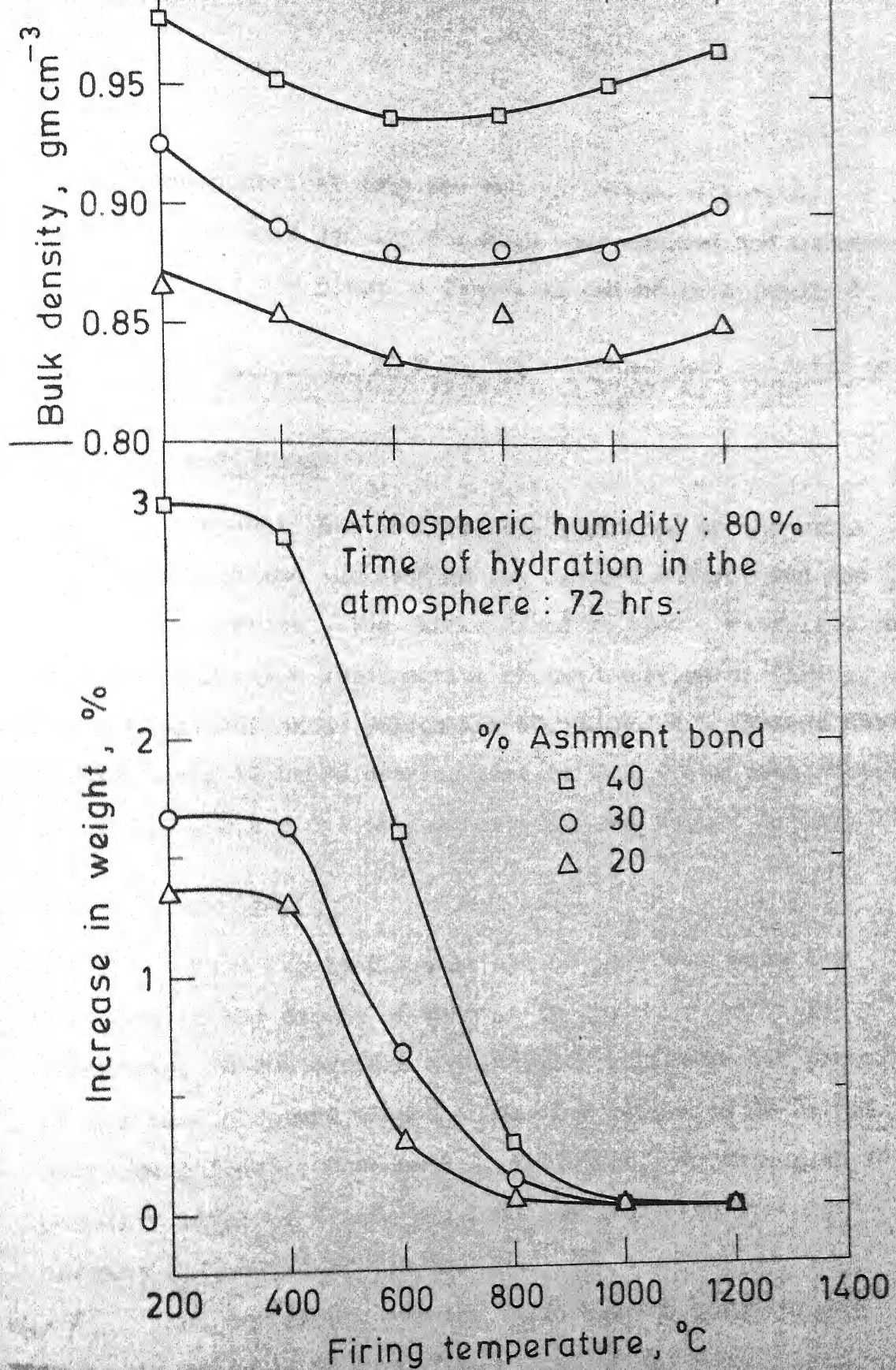


Fig. 6.3.3 - Variation in bulk density and hydration as a function of firing temperature for ashmen bonded rice husk ash insulation discs.

The numerical data for the shrinkage, strength, hydration and bulk density for both hand moulded and machine pressed bricks are given in Tables A5 and A6 in Appendix-1.

6.3.2. EFFECT OF SOAK TIME ON THE SHRINKAGE AND POROSITY OF THE ASHMENT BONDED INSULATIONS FIRED AT 1200°C

6.3.2.1. SHRINKAGE

As mentioned earlier, the shrinkage of the brick increases with the increase in the ashment content and the firing temperature. The bricks fired at 1200°C exhibited near constant shrinkage irrespective of the duration of firing. The average shrinkage values for 40, 30 and 20% ashment bond bricks, over 12 hours soaking time at 1200°C has been observed to be 3.65, 2.0 and 1.5% respectively (see Figure 6.3.4).

6.3.2.2. POROSITY

From Figure 6.3.4 it can be seen that with the increase in the amount of ashment in the brick porosity decreases. A 20% ashment bonded brick will have 64% porosity. It has been observed that the porosity decreases by 2% for every additional 10% ashment in the brick. No change in the porosity level of bricks has been observed with prolonged heating (12 hours) at 1200°C.

The numerical data for shrinkage and porosity are given in Table A7 in Appendix-1.

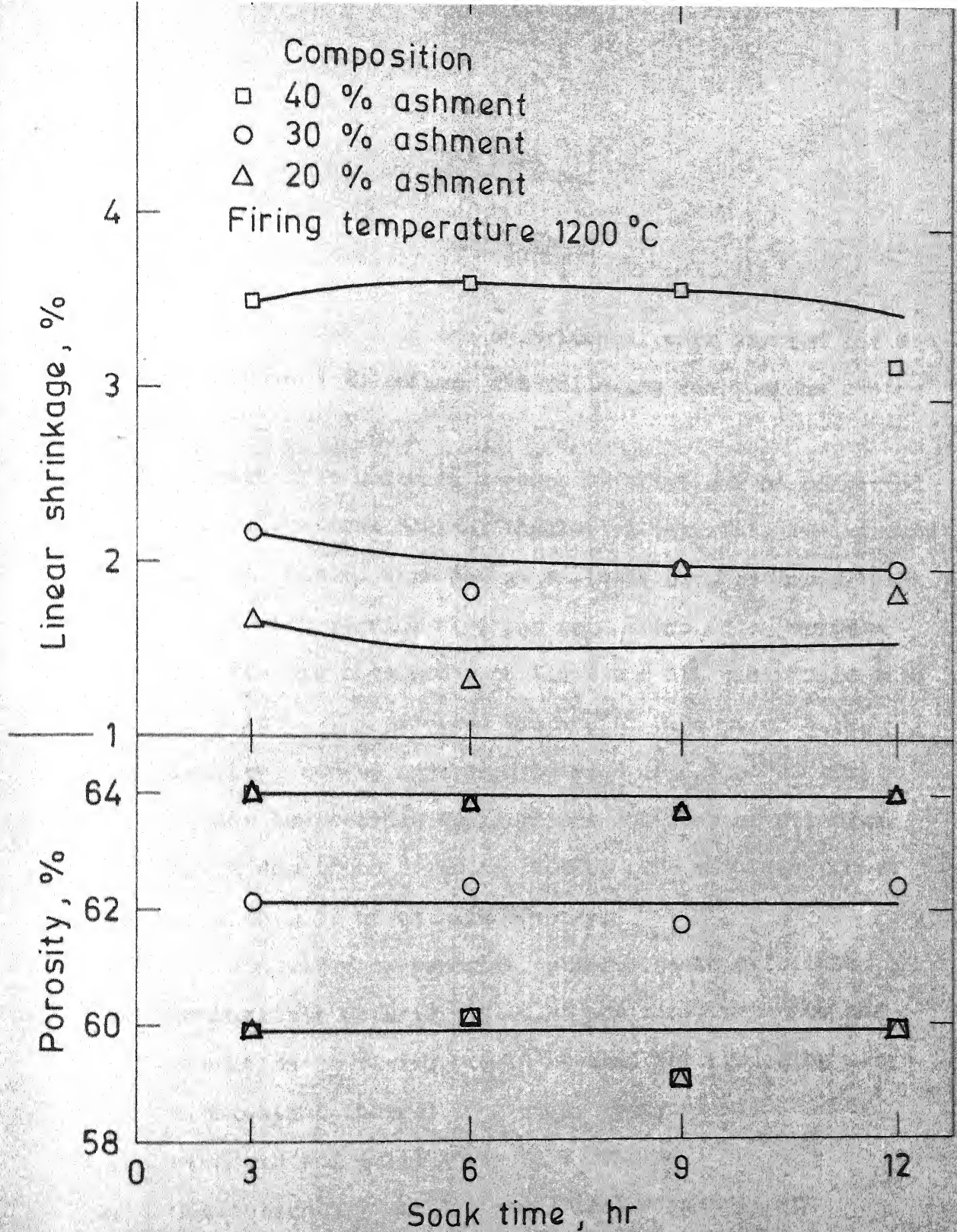


Fig. 6.3.4- Variation of porosity and shrinkage as a function of soak time for ashment bonded rice husk ash insulation discs at 1200 °C.

CHAPTER - 7

CONCLUSIONS

On the basis of the experimental work carried out and results obtained therefrom, the following conclusions can be drawn:

1. Thermit slag which is a waste material can be converted into ultralight thermal insulating material. The ground slag is bonded with sodium silicate or phosphoric acid bonds with varying slag/pop corn ratio (Z). Optimum results are obtained with 1.5 Z and 40% phosphoric acid solution. The prefired brick with 0.34 gm/cc bulk density, can be conveniently used upto 1000°C. For higher temperature applications and greater strength, brick should be fired to 1200°C. The resulting brick is with 0.37 gm/cc bulk density.

In place of pop corn, other organic exfoliated combustible materials such as pop rice, with low gas formation on firing, could be used for producing ultralightweight thermal insulating material with higher strength and still lower bulk density.

2. Conventionally mullite insulating materials are manufactured from kyanite, sillimanite base materials or from mullite itself with external combustible materials for introducing porosity. Whereas in the present work, it has been shown that it is possible

to develop mullite insulating brick with about 60% porosity, negligible dimensional change and high strength at higher temperatures using a waste material, rice husk ash, which provides both a reactive silica and high porosity. These insulations can be used upto 1500°C or more.

3. Ashment bonded rice husk ash insulating materials developed in this work, can be used from room temperature to 1200°C, either in the form of pressed blocks or as a ramming mass. The shrinkage and strength values are best suited for nonload bearing insulating application. These bricks exhibited above 60% porosity for the bricks fired at 1200°C for varying time periods. The adoption of this exceptionally cheap and simple insulations do not need any technical expertise in using as an insitu insulating material in a high temperature furnace for either roof or side walls.

REFERENCES

1. Chesters, J.H., Refractories Production and Properties, The Iron and Steel Institute, 1973.
2. P.C. Aitcin and M. Cossette, "Lightweight Concretes with Aggregates Made from Asbestos Mine Tailings", CIM Bulletin, Dec. 1979, p. 95.
3. P.C. Kapur, "Thermal Insulations from Rice Husk Ash, An Agricultural Waste", Ceramurgia Int., Vol. 6, No. 2, 1980, p. 75.
4. E.C. Beagle, "Rice-Husk, Conversion to Energy", FAO Agricultural Bulletin 31, Rome 1978, Ch. 3, "Physical and Chemical Characteristics of Rice Husk", pp. 25-28.
5. S. Hanafi and S.A. Abo-El-Enein, "Surface Properties of Silicas Produced by Thermal Treatment of Rice Husk Ash", Thermochemica Acta, 37, 1980, pp. 137-143.
6. D.M. Ibrahim, S.A. El-Hemaly and F.M. Abdelkerim, "Study of Rice Husk Ash Silica by Infrared Spectroscopy", Thermochemica Acta, 37, 1980, pp. 307-314.
7. Robert F. Davis and Joseph A. Pask, "Mullite", High Temperature Oxides, Part-4, ed. Allen M. Alper, 1971, p. 37.
8. Stately, W.G. and Brindley, "Development of Non-crystalline Material in Subsolidus Reactions between Silica and Alumina", J. Am. Ceram. Soc., 36, 1969, p. 616.
9. Singer, F. and Singer, S.S., "Industrial Ceramics", Chapman and Hall, London, 1963.
10. Kappmeyer, K.K. and Manning, R.H., "Evaluating High-Alumina Brick", Am. Ceram. Soc. Bull., 42, 1963, p. 105.
11. Gupta, H.K., "Optimization of Manufacturing Parameters for Ashmoh Cement", M.Tech. Thesis, Dept. of Metallurgical Engg., I.I.T. Kanpur, August 1978.
12. Petzold, A. and Rohrs, M., "Concrete for High Temperatures", MacLaren and Sons, London, 1970, p. 21.
13. P.C. Kapur and A.S.R. Sai, "Ashment Cement", Internal Report, I.I.T., Kanpur.

14. K. Fisher, "Chemical Bonds for Refractory Materials", Proc. Brit. Ceram. Soc., No. 12, pp. 51-64, March 1969.
15. Martin J. O'Hara, Jules J. Duga and Herbert D. Sheets, Jr., "Studies in Phosphate Bonding", Am. Ceram. Soc. Bull., 51(7), 1972, pp. 590-595.
16. A.K. Roy and N.R. Sircar, "Phosphate Bonding of Aluminous Aggregates and Thermo-Mechanical Characterisation of Monolithics", Tran. Indian Ceram. Soc. 6, Nov.-Dec. 1978, pp. 236-241.
17. John E. Cassidy, "Phosphate Bonding Then and Now", Am. Ceram. Soc. Bull., 56(7), 1977, pp. 640-643.
18. Robert B. Sosman, "The Phases of Silica", Rutgers University Press, 1965, p. 148.

APPENDIX-1EXPERIMENTAL MEASUREMENTS

Table A1. Variation of Bulk Density as a Function of Z Value for Sodium Silicate Bonded Thermit Slag Lightweight Insulations Fired at 800°C.

S. No.	Slag (gms)	Pop Corn (gms)	Slag/Pop Corn Ratio (Z)	Bulk Density (gm/cc)
1	90	60	1.50	0.4883
2	90	45	2.00	0.6957
3	180	80	2.25	0.8506
4	180	70	2.57	0.8974
5	180	65	2.75	0.9874
6	180	45	4.00	1.0930
7	120	25	4.80	1.1790
8	180	35	5.14	1.1680
9	180	30	6.00	1.2270

Table A1. Shrinkage and Bulk Density Values for Lightweight Insulation Bricks Fixed to Different Temperatures for 3 hours.

Temperature (°C)	Sample No.	Initial Dimensions			Final Dimensions			% Diametric Shrinkage	% Height Shrinkage	% Volumetric Shrinkage	Bulk Density (gm/cc)
		D ₂	H ₂		D ₃	H ₃					
1000	10	6.100	3.180		6.100	3.150		0	0.94	0.60	0.35
	11	6.150	3.280		6.150	3.140		0	4.26	4.86	0.36
	12	6.010	3.320		6.000	3.240		0	2.40	2.60	0.35
1100	7	6.178	3.292		6.110	3.150		1.10	4.30	5.67	0.40
	8	6.100	3.300		6.150	3.150		0.81	4.50	3.00	0.35
	9	6.220	3.320		6.200	3.070		0.90	7.50	8.11	0.36
1200	1	6.275	3.330		6.110	2.930		2.63	12.00	16.40	0.39
	2	6.281	3.365		6.130	3.000		2.40	10.85	14.00	0.36
	3	6.235	3.270		6.150	3.000		1.36	8.25	10.50	0.36
1300	4	6.309	3.380		5.780	2.630		8.38	22.20	34.60	0.50
	5	6.310	3.327		5.870	2.730		6.97	17.95	25.60	0.50
	6	6.068	3.548		5.700	2.750		6.07	22.50	31.60	0.48

Table A3. Composition and Bulk Density Values for Hollow Bubbles Made from Thermit Slag.

Bond	Amount of Bond (ml)	Fire Clay (%)	Slag (gm)	Pop Corn (gm)	Z	Bulk Density			Code
						800°C		1200°C	
						Loose	Tap	Loose	Tap
Sodium Silicate (sol) (1.3, sp. gr.)	45	5	160	80	2.00	0.3373	0.3600	--	B II C
	64	10	200	80	2.50	0.4290	0.4560	--	B II b
Sodium silicate (sol) (1.4, 5 sp. gr.)	50	5	150	100	1.50	0.2600	0.2990	0.2860	0.3290 A II a
	30	5	50	40	1.25	0.3580	0.3830	--	A I a
50% Phosphoric acid (sol)	27	10	50	40	1.25	0.2096	0.2421	0.3852	0.4118 B I a

Table A4. Variation of Shrinkage, Porosity and Tensile Strength for Mullite Insulation Discs Fired at 1450°C, with Time.

Soak Time (Hours)	% Shrinkage			% Porosity			Tensile Strength (kg/cm ²)		
	Composition			Composition			Composition		
	CM	FM	3 PFM	CM	FM	3 PFM	CM	FM	3 PFM
2.0	---	---	---	58.1	52.1	50.5	---	---	---
4.0	---	---	---	58.1	52.1	50.8	---	---	---
6.0	---	---	---	57.9	52.0	51.0	---	---	---
8.5	7.5	6.2	4.7	57.7	51.9	51.2	7.24	16.95	15.79
17.0	7.7	6.9	5.6	57.3	51.7	51.4	8.43	20.16	18.00
25.5	8.2	7.0	5.7	57.3	51.3	51.6	9.03	24.35	16.10
34.0	8.0	7.0	5.8	57.3	51.3	51.8	8.80	27.34	18.16

Table A5. Variation of Shrinkage, Compressive Strength and Hydration with Firing Temperature for Hand Moulded, Ashment Bonded Rice Husk Ash Insulation Cubes.

Firing Temperature (°C)	% Shrinkage			Compressive Strength (kg/cm ²)			% Hydration		
	% Ashment Bond			% Ashment Bond			% Ashment Bond		
	20	30	40	20	30	40	20	30	40
Room Temp.				12.6	13.8	15.0			
200	0.175	0.36	0.24	5.2	9.0	11.6	1.34	1.630	2.980
400	0.370	0.24	0.10	4.8	6.8	8.0	1.25	1.620	2.850
600	0.390	0.34	0.60	3.8	5.0	12.8	0.31	0.860	1.626
800	1.577	0.80	1.43	7.0	6.0	14.2	0.02	0.117	0.281
1000	1.970	2.20	1.82	10.8	12.4	9.8	0	0	0.035
1200	2.020	2.28	2.82	16.8	19.6	21.7	0	0	0.010

Table A6. Variation of Shrinkage, Tensile Strength and Bulk Densities with Firing Temperature for Machine Pressed, Ashment Bonded Rice Husk Ash Insulation Discs.

Firing Temperature (°C)	% Shrinkage			Tensile Strength (kg/cm ²)			Bulk Density (gm/cc)		
	% Ashment Bond			% Ashment Bond			% Ashment Bond		
	20	30	40	20	30	40	20	30	40
Room Temp.	-	-	-	0.60	1.26	2.31	-	-	-
200	0.14	0.148	0.360	0.63	0.89	1.34	0.865	0.926	0.977
400	0.31	0.646	0.606	0.40	0.77	1.13	0.854	0.890	0.952
600	0.53	0.783	0.910	0.39	0.59	0.90	0.835	0.880	0.937
800	0.64	1.210	2.140	0.92	0.99	1.24	0.854	0.882	0.938
1000	1.02	1.890	2.430	2.45	2.64	2.40	0.837	0.885	0.952
1200	1.35	2.100	3.500	7.86	7.87	18.85	0.850	0.902	0.969